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Palaeontology and Zoölogy. — "*Phylogenetic and Ontogenetic Increase of the Volume of the Brain in Vertebrata*". By Prof. EUG. DUBOIS.

(Communicated at the meeting of June 24, 1922).

One of the most striking and important palaeontological facts ever brought to light in the investigation of the strata of the earth, is that of the extremely slight volume which the encephalon possesses in the earliest forms of Reptiles, Birds and Mammals. By this feature do these for the rest very differentiated and often gigantic earliest representatives of their class differ from the forms immediately following them and from the modern ones, in a way which must almost seem ridiculous to the comparative anatomist.

As regards Reptiles this has especially become known, by the discoveries of MARSH, about the Dinosauria, the principal terrestrial animals of the Mesozoic Era. In them the spinal canal, in its whole length, was not seldom wider than the cranial cavity. In *Stegosaurus*, from the Lowest Cretaceous in Wyoming, the cross-section of the sacral enlargement of the spinal canal (this in connection with the large hind-legs) was ten times as large as the cranial cavity. In a *Diplodocus* of a computed body length of 24 meters, from the same strata, this cavity is only 9 cm. long and 5 cm. wide, whereas that of an adult alligator, with a tenth of that maximum body length of its mesozoic distant relation, has a length of $6\frac{1}{2}$ cm. and a width of 3 cm. Also in *Theromorpha* and *Pterosauria* the cranial cavity is very small.

Ichthyornis, described by MARSH from the Upper Cretaceous of Kansas, possessed only the third of the cranial capacity of the Large Sea Swallow (*Sterna cantiaca*), with which this toothed Mesozoic bird bore considerable resemblance in size and structure of its skeleton, probably also the mode of life of the two birds was similar.

In the class of the Mammalia, the Eocene primitive Carnivora, the *Creodontia*, possessed very little encephalon, which appears clearly on comparison of the cast of the brain-cavity of *Arctocyon*, from the Basal Eocene of Reims, with that of a dog of similar size of body (Fig. 1, A). The *Condylarthra* from the Lower Eocene, from which the existing sub-orders, the *Perissodactyla* and *Artiodactyla*

both originated, had also brains of incomparably small volume; side by side with the brain cast of *Phenacodus*, from the Wasatch Formation of Wyoming, that of a pig of similar size of the body appears as gigantic (Fig. 1, B). Also other Eocene Hoofed Mammalia, the Amblypoda, had very small brains. Thus *Coryphodon*, from the Wasatch Formation, in comparison with a *Rhinoceros* of similar size (Fig. 1, C).

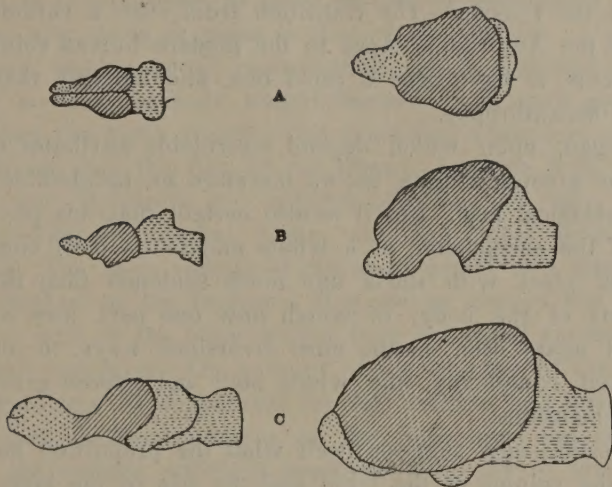


Fig. 1. Brain cast of: A. *Arctocyon* and *Canis*; B. *Phenacodus* and *Sus*; C. *Coryphodon* and *Rhinoceros*. (After OSBORN¹⁾).

In all these cases the most compounded, functionally most intricate parts of the encephalon, especially the cerebrum (hatched in Fig. 1), have the smallest volume. They in particular have not yet come to a fuller growth. But in the Miocene, partly already in the Eocene Period, the brain in the Mammalia reaches the volume and the proportion of its sub-divisions of most modern types.

As remarkable as this sudden, at all events comparatively rapid increase of the volume of the brain in the classes of Reptiles, Birds, and Mammals is the other paleontological fact, that in the Hominides, which geologically do not appear until very late, the brain immediately possessed the same volume already in the earliest of the known crania as in modern ones. The expectation that by means of these skulls a gradual increase of the volume of the brain might be shown, up to the exceptional capacity whose possession raises

¹⁾ H. F. OSBORN, The Age of Mammals in Europe, Asia and North America, p. 173. New York 1910.

modern Man so high above the animals, has not been realized. This however does not apply to *Pithecanthropus*, if this fossil anthropomorphous Primate is not considered to be of a separate family, but reckoned to belong to the Hominides. For he possessed only *two thirds* of the cerebral volume of the Australian aboriginal (which he resembled in body size and also in the main features of his skeleton), but *twice* that of anthropoid apes of the same body size. But also this "precursor of Man" is of a late date — probably not before the Pliocene. The transition from such a volume of brain as that of the Anthropoid Apes to the modern human volume seems at all events to have been a rapid one, and halfway there is still that of *Pithecanthropus*.

This organ, upon which depend inscrutable attributes of animal life, of the greatest degree, shows therefore an indubitable progress in the geological past. But it is also certain that this phylogenetic growth of the encephalon, as a whole and in its most compounded parts, took place with starts, and much seldomer than that of the other parts of the body, of which now one part, now another is again and again seen, in the most diversified ways, to increase in volume and complexity, the whole body not seldom growing into gigantic dimensions.

The question now suggests itself what the proportion has become between the volume of the brain and the size of the body through phylogenetic and ontogenetic growth, i. e. increase from species to species and from individual to individual, in adult animals of the present time.

It can easily be ascertained that the brain volume, reached by a species of animals in adult state, depends both on the size of the body and on the stage of development attained by the brain, which determines the degree of the functions of the organ.

It is not astonishing that the absolute brain weight of Man is surpassed by that of the Elephant and the large whale species. The largest whale species, which is a thousand times heavier than Man, possesses five times his brain weight. It is also self-evident that such a gigantic species of the cat family as the Tiger has much larger brain than the Domestic Cat; to sixty-four times the body weight of the latter, the Tiger has ten times its brain weight. Keeping to the same species we find in an adult dog of the size of the Wolf, of about 40 kg. body weight, double the brain weight of a lap-dog weighing about 2 kg.

But besides on the size of the body, the brain volume depends also on the stage of development of this organ, on the particular

structure and functions of other organs, and on other not easily measurable factors which determine the cephalisation of the central nervous system. When we compare Man with animals of the same body weight, when, in other words, we eliminate the factor body weight, we see that he far surpasses all the animals. He possesses three times the brain weight of a species of anthropoid apes of the same weight and more than six times that of an equally heavy gazelle. We may also say that the coefficient of cephalisation κ of Man is three times as great as that of Anthropoid Apes and more than six times as great as that of the Gazelle.

We may assume equal cephalisation for the Cat and the Tiger, and yet we see the body weight increase in a much greater proportion than the brain weight. The same fact is found on comparison of the Mouse with the Rat, of the Pigmy Antelope with the Beisa-Antelope etc. Evidently the weights of brain and body, also with equal development of that organ, are not simply proportional to each other. The large species of the same genus, and also the large adult individual of the Domestic Dog species always has less brain weight in ratio to the body weight than the small species and the small adult individual. On account of the equality of the densities, the volumes may be substituted for the weights, and it is, therefore, possible that another measure of the body than the volume, for instance the surface, which is proportional to the $2/3$ power of the volume, — for which the weight P of the large animal may be put, and the weight p of the small one, — determines the quantity of brain — volume or weight — of the species. A priori it seems, indeed, that there is a good deal to be said for this view, for the sensual areas, the physiological cross-sections of the muscles, which determine muscular force, the superficial extent of the body, on which metabolism depends, are proportional to the surface of the body. The brain weights E and e of two animals differing only in body weight, but with for the rest quite identical organisation, may always be put $E = \kappa P^r$ and $e = \kappa p^r$; then the exponent of relation r , indicating the power of the body weight with which the brain weight increases or decreases, can be calculated from the equation $r = \frac{\log E - \log e}{\log P - \log p}$ and $\kappa = \frac{E}{P^r}$ will be found.

Twenty-five years ago, making use of the observations of weight published by MAX WEBER ¹⁾ a year before, I found thus $5/9$ as mean

¹⁾ MAX WEBER, Vorstudien über das Hirngewicht der Säugethiere, in Festschrift für CARL GEGENBAUR, p. 105—123. Leipzig 1896.

value of r in seven pair of mammalian species, i.e. a slightly smaller exponent than would correspond to the proportionality of the brain weight with the surface dimensions of the body¹⁾. The discrepancy appeared to be constant, and the same exponent was found for Birds by LOUIS LAPICQUE and PIERRE GIRARD in 1905²⁾, and for Reptiles and Fishes by me in 1913³⁾. The exponent $\frac{5}{9}$ holds undoubtedly for all Vertebrata. Certainly this "strange power" of the body weight cannot be attributed to insufficiency of the data; it is impossible that we have to do here with a "rough empirical law, as limit of a sum of different functions". The relation found between the weights of the brain and the body must be a simple, rational one. As this exponent indicates the relation of species to species, a relation which must have come about with the origination of the species, I will designate it here as phylogenetic exponent.

In the system of coördinates of Fig. 2 the body weights in kg.

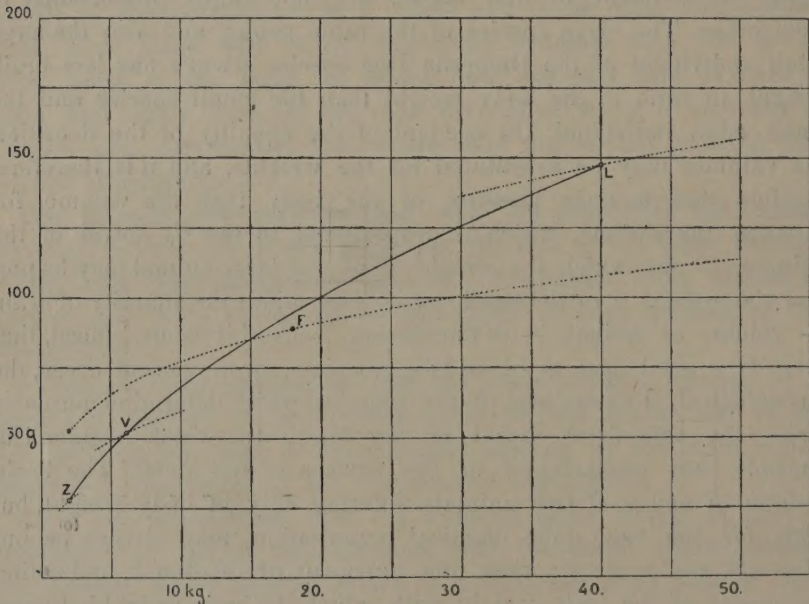


Fig. 2

1) Eug. Dubois, De verhouding van het gewicht der hersenen tot de grootte van het lichaam bij de Zoogdieren. Verhandelingen der Kon. Akademie van Wetenschappen te Amsterdam. Tweede Sectie. Deel V, N^o. 10. 1897. — Also: Sur le rapport du poids de l'encéphale avec la grandeur du corps chez les Mammifères, in Bulletins de la Société d'Anthropologie de Paris 1897, p. 337—376.

2) Comptes Rendus des séances de l'Académie des Sciences. Paris 1905, 1, Tome 140, p. 1057—1059.

3) These Proceedings, Vol XVI, p. 651—654. 1914.

are indicated on the abscissa, the brain weights in gr. on the ordinate. The points *Z*, *V*, *F*, and *L* refer to the averages of those weights of the species *Canis zerda*, *Canis vulpes*, *Canis familiaris* and *Canis lupus*. The relation of brain weight and body weight in these species of the genus *Canis* is here graphically represented by the full exponential curve *ZVL*, defined by the equation $E = 0.41 P^{.5}$, and by the point *F*, whose position is defined by the equation $89 = 0.385 \times 18000^{.5}$. In Fig. 3 the same relation is

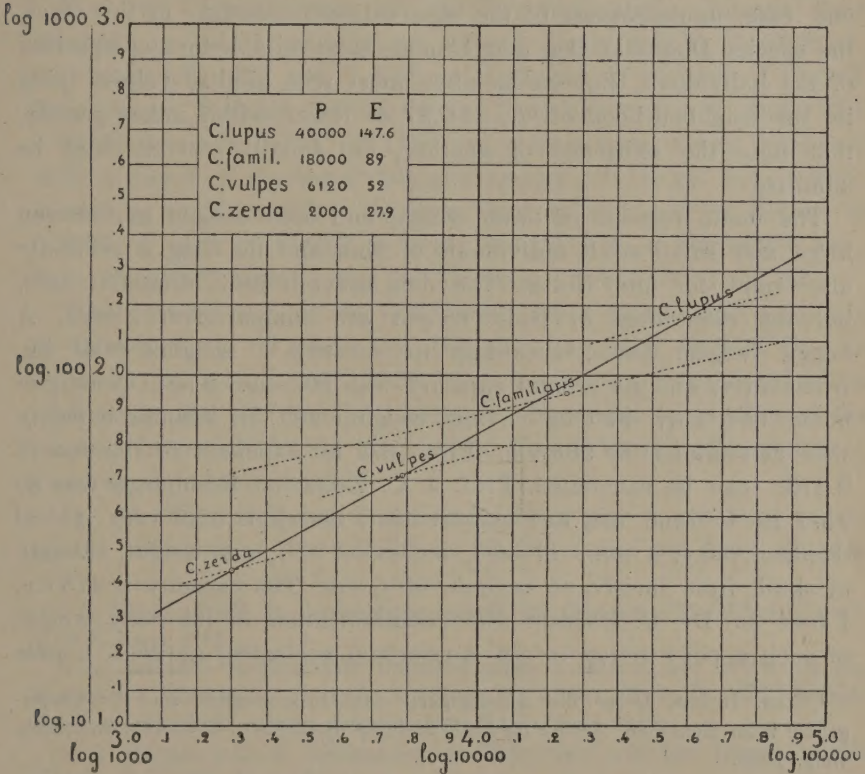


Fig. 3

represented by the full logarithmic line, a straight line with which the lines of genera and species with other cephalisation would run parallel.

An entirely different exponent of relation, viz. about $\frac{1}{4}$, i.e. less than $\frac{5}{18}$, half the value of the exponent holding from species to species, was found on comparison of large adult individuals of one and the same species by LAPICQUE for the Domestic Dog ¹⁾ in 1898,

¹⁾ L. LAPICQUE, Sur la relation du poids de l'encéphale au poids du corps. Comptes rendus de la Société de Biologie. Paris 1898, p. 63.

and independently of the distinguished French physiologist, in the same year, by me for Man¹⁾. In 1907 this result was confirmed by LAPICQUE²⁾ for Man; at present, from the new observations of weight on 150 Berlin dogs by BERTHOLD KLATT³⁾ I can corroborate the result obtained by LAPICQUE from RICHTER's 188 Paris dogs⁴⁾.

Similar low interindividual exponents of relation as for Man and the Domestic Dog are now also valid within other species. For obvious reasons: very important differences of the body weights in one case, numerousness of the observations of weight in the other, the species Domestic Dog and Man are most suitable for a comparison of the individuals. But we so often meet with similar values, lying in the neighbourhood of $\frac{5}{18} = 0.27$ or lower, within other species, that here the existence of another, but equally real law may be admitted.

The same relation of brain weight and body weight as between large and small adult individuals of Man and the Dog is certainly also valid for the Horse. The data are not very numerous here, but the differences in body weight are comparatively large. A heavy Belgian horse, according to CORNEVIN⁵⁾, weighed 1040 kg. when alive, and its cranial capacity was 805 c.c.; a light Camargue horse had only 320 kg. living weight, and its cranial capacity was determined at 585 c.c. From this an exponent of relation of 0.2708 can be calculated. Prof. J. C. EWART at Edinburgh was so kind as to send me, for measurement, the skull of a very typical Shetland pony, a mare of $36\frac{1}{2}$ inches or $92\frac{1}{2}$ cm. height. Length of skull, from incisivi to occiput, $40\frac{1}{2}$ cm. The capacity is 475 c.c. I owe to Dr. C. KERBERT the communication of the body weight of such a pony living in the Amsterdam zoological gardens, a male

¹⁾ EUG. DUBOIS, Ueber die Abhängigkeit des Hirngewichtes von der Körpergrösse beim Menschen. Archiv für Anthropologie. Band 25, p. 423—441. Braunschweig. 1898.

²⁾ L. LAPICQUE, Le poids encéphalique en fonction du poids corporel entre individus d'une même espèce. Bulletins et mémoires de la Société d'Anthropologie de Paris. Séance du 6 Juin 1907. 5^{me} Série, Tome 8, p. 315. Paris 1908.

³⁾ BERTHOLD KLATT, Studien zum Domestikationsproblem. Untersuchungen am Hirn. Bibliotheca Genetica (E. BAUR). Band II. 180 pag. My calculations are to be published in Bijdragen tot de Dierkunde. XXII. Hat sich das Gehirn beim Haushunde, im Vergleich mit Wildhundarten, vergrössert, oder verkleinert? Leiden 1922.

⁴⁾ CHARLES RICHTER, Poids du cerveau, de la rate et du foie, chez les Chiens de différentes tailles. Physiologie. Travaux du Laboratoire de M. CHARLES RICHTER. Tome Deuxième, p. 381—397.

⁵⁾ CH. CORNEVIN, Examen comparé de la capacité crânienne dans les diverses races des espèces domestiques. Journal de médecine vétérinaire et de zootechnie, publié à l'École de Lyon, 3^{me} Série, Tome 14, p. 24. 1889.

horse of the same height (92 cm.) and skull length (41 cm.); it was 128 kg. By comparison with CORNEVIN's heavy Belgian horse I now find an exponent of relation of 0.2528. The heaviest of 15 male horses, according to COLIN¹⁾, a Percheron of 501 kg. dead weight, compared with the lightest male horse ("de petite taille") of this group, of 288 kg. dead weight, gives an exponent of relation of 0.1855. The heaviest horse was probably less emaciated than the lightest; hence the exceedingly low exponent.

For two groups, each of six domestic rabbits, formed from MÜLLER's records²⁾, one of an average body weight of 4386 gr., the other of 1727 gr., I find an exponent of relation of 0.2512. Two groups, each of five male moles, from MANOUVRIER³⁾, yield 0.234.

Eight domestic ducks, of 1756 gr. average body weight, compared with a dwarf of the same domestic species, of 755 gr. body weight, according to TIMMANN's⁴⁾ records, yield an exponent of relation of 0.3096. A cock of 1745.7 gr. body weight with a hen of 985.2 gr., from FALCK's⁵⁾ report, yield an exponent of relation of 0.2248.

Two groups, each of six Bull Frogs (*Rana catesbyana*), according to DONALDSON⁶⁾, of 244.5 and 164 gr. mean body weight, give an exponent of relation of 0.2516. Also the average cranial capacities of 9 male and 11 female Australian aborigines in relation to the mean volumes of the six long bones, from HAUGER's observations⁷⁾, yield an exponent of 0.2770.

In the Figures 2 and 3 the dotted lines give a graphical record of the relations of the weights of the brain and the body between

¹⁾ G. COLIN, *Traité de physiologie comparée des animaux*. 3^{me} Édition, Tome I, p. 302. Paris 1886.

²⁾ E. MÜLLER, *Vergleichende Untersuchungen an Haus- und Wildkaninchen*. Zoologische Jahrbücher. (Spengel). Abteilung für Allgem. Zoologie und Physiologie der Tiere. Band 36, p. 585. Gesamttabelle XXVa. Jena 1919.

³⁾ L. MANOUVRIER in *Dictionnaire de Physiologie* par CH. RICHTER, article „Cerveau", p. 680. Paris 1898.

⁴⁾ O. TIMMANN, *Vergleichende Untersuchungen an Haus- und Wildenten*. Zoologische Jahrbücher, *ibid.*, p. 653.

⁵⁾ C. PH. FALCK, *Beiträge zur Kenntnis der Bildungs- und Wachstumsgeschichte der Thierkörper*. Schriften der Gesellschaft zur Beförderung der gesamten Naturwissenschaften zu Marburg. Band 8, p. 242. Marburg 1857.

⁶⁾ H. H. DONALDSON, *On a Formula for Determining the Weight of the Central Nervous System of the Frog from the Weight and Length of its Entire Body*. University of Chicago. Decennial Publications. Vol. 10. (1902), p. 7.

⁷⁾ OTTO HAUGER, *Der Gehirnreichtum der Australier und anderer Hominiden, beurteilt nach ihrem Skelet*. Anatomische Hefte (MERKEL und BONNET). I. Abteilung. Heft 179. Band 59, p. 589: Tabelle I, p. 616—617: Tabelle III. München und Wiesbaden 1921.

adult individuals of four species of the genus *Canis*. In Fig. 2 they are again exponential curves, defined, for the Domestic Dog, by the equation $E = f P^{0.24} = 8.475 P^{0.24}$ (in which f is found from $89 = f \times 18000$), and for the wild Canidae, $E = 4.615 P^{6/18}$ (in which $4.615 = \frac{52}{6120^{6/18}}$). In Fig. 3 they are straight lines, both of them less steep than the lines for these relations from species to species, which they intersect in the points of the means, as far as the wild species are concerned. I have derived the mean point for the Domestic Dog, and the line for the individual relation, within this species from observations of weight on 434 dogs, i. e. 152 new ones by KLATT ¹⁾, RICHET's 188 observations ²⁾, LAPICQUE and DHÉRE's 47 ³⁾, RÜDINGER's 19 ⁴⁾, WILDER's 16 ⁵⁾, MAX WEBER's 12 ⁶⁾. On the ground of these data 18 kg. may be admitted for the mean weight of the Domestic Dog, 89 gr. for its mean brain weight. The brain weight is certainly at least 6%, probably 10% lower than in a wild species of *Canis* of the same weight. This can only be considered as a consequence of domestication, i. e. of unnatural mode of living. Something of the same kind was found by DONALDSON and HATAI ⁷⁾ in the domesticated albino-form of the Brown Rat (*Mus norvegicus*). Not only the body weight has been reduced in this domestic Rat, but the brain weight comparatively to a greater degree, a phenomenon of domestication due to a diminished growth of the brain, which was already known to DARWIN (1868) for the domestic Rabbit ⁸⁾, and which was afterwards confirmed by LAPICQUE ⁹⁾, KLATT ¹⁰⁾, and

¹⁾ B. KLATT, l.c. Haupttabelle at the end of his work.

²⁾ CH. RICHET, l.c.

³⁾ L. LAPICQUE in Bulletins et mémoires de la Société d'Anthropologie de Paris 1907, p. 316.

⁴⁾ N. RÜDINGER, Ueber die Hirne verschiedener Hunderassen. Verhandlungen der Anatomischen Gesellschaft. Jena 1894. Ergänzungsheft zum 9. Band (1894) des Anatomischen Anzeigers, p. 173—176.

⁵⁾ B.-G. WILDER, Cerebral Variation in Domestic Dogs. Proceedings of the American Association for the Advancement of Science, 22nd Meeting (1873), p. 235—236. Salem 1874.

⁶⁾ MAX WEBER, Vorstudien über das Hirngewicht der Säugethiere l.c., p. 112.

⁷⁾ H. H. DONALDSON and SHINKISHI HATAI, A Comparison of the Norway Rat with the Albino Rat. Journal of Comparative Neurology. Vol. 21 (1911), p. 417—458, particularly p. 454—455.

⁸⁾ CH. DARWIN, The Variation of Animals and Plants under Domestication. Chap. IV.

⁹⁾ L. LAPICQUE in Bulletins et mémoires de la Société d'Anthropologie de Paris 1907, p. 331—337: „Régression cérébrale des animaux domestiques”.

¹⁰⁾ B. KLATT, Ueber die Veränderung der Schädelkapazität in der Domestikation. Sitzungsberichte der Gesellschaft Naturforschender Freunde zu Berlin. 1912, p. 155.

MÜLLER¹⁾. The same cerebral regression by domestication was found by LAPICQUE²⁾ for the Ox and the Sheep, by KLATT³⁾ and BETHCKE⁴⁾ for the Ferret, by LAPICQUE⁵⁾ and TIMMANN⁶⁾ for the domestic Duck, and now by me for the Domestic Dog. For 72 of DONALDSON and HATAI's wild *Mus norvegicus*⁷⁾ of both sexes, of 335 to 525 gr., averagely 389.861 gr. body weight, with averagely 2.402 gr. brain weight, and 71 male and female wild rats of 275 to 325 gr., averagely 300.211 gr. body weight, with an average brain weight of 2.299 gr., I calculate an exponent of relation of 0.1674. That this exponent is considerably smaller than is usually found between individuals of one species, may be readily explained in this way that DONALDSON and HATAI give the body weights irrespective of the state of adolescence and the fat percentage (of which they state that it augments with age); part of the increase of the body weight is, therefore, not accompanied by increase of the brain weight, as is the case on comparison of adult individuals only, and which are in a medium condition.

In Fig. 4, after DONALDSON⁷⁾ the exponent of the individuals with body weights between 250 and 446 gr. may be calculated at 0.1572 for the male wild *Mus norvegicus* (from observations of weights on 232 male specimens of all ages). From DONALDSON's Table 85⁸⁾ the exponent 0.1554 may be calculated for body weight of 301.0 to 389.7 gr. The exponent is 0.1342 for the male albino of this species of 181 to 350 gr. body weight. The relatively smaller increase of the brain weight with increasing body weight of the (domestic) albino Rat finds expression in the slower ascent of the curve and the lower value of the exponent. It may be admitted that the exponent is in general somewhat lower in the domesticated species (not leading a natural life), because the brain increases somewhat

¹⁾ E. MÜLLER, Vergleichende Untersuchungen an Haus- und Wildkaninchen. Loc. cit. p. 503—588.

²⁾ See note 9 foregoing page.

³⁾ See note 10 foregoing page.

⁴⁾ H. BETHCKE, Vergleichende Untersuchungen an Frettchen und Iltissen. Ibid., p. 589—620.

⁵⁾ O. TIMMANN, Vergleichende Untersuchungen an Haus- und Wildenten. Ibid., p. 621—656.

⁶⁾ DONALDSON and HATAI, l.c., p. 426—427.

⁷⁾ From Chart 31, p. 201 in H. H. DONALDSON, The Rat. Reference Tables and Data for the Albino Rat (*Mus norvegicus albinus*) and the Norway Rat (*Mus norvegicus*). Memoirs of the Wistar Institute of Anatomy and Biology. N^o. 6. Philadelphia 1915.

⁸⁾ Ibid, p. 208.

less under these circumstances, in proportion to the body weight grows in a less degree than in the natural state.

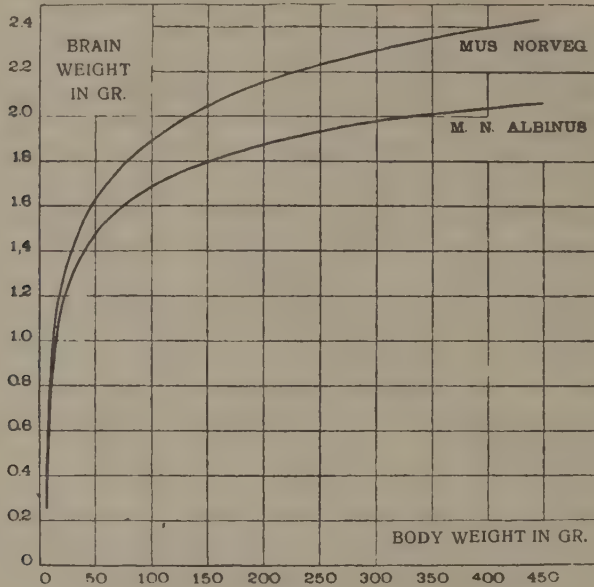


Fig. 4.

In 1918 I found an exponent of $\frac{5}{18} = 0,27$, i.e. of precisely half the value of the exponent holding for the relative brain weights from species to species, on comparison of the volumes of largest, i.e. of full-grown, homologous nerve or ganglion cells in relation to the body weights of adult animals of very different sizes, both of one species and of different species. Compare Tables I and II¹⁾.

Though in the microscopical image of the grey cortex the nerve cells are placed as densely and are as unequal in size as the stars in the telescopic image of the Milky Way, we may yet admit a relation between the average size of these cells and the size of the body, and look for the explanation of the relation holding for the volume of the brain in the nerve cells, the elements from which the brain is composed.

The exponent holding between the adult individuals of one and the same species, in the relation of the body weight to the brain weight, may now be distinguished as ontogenetic exponent from

¹⁾ These Proceedings, Vol. XX, p. 1328—1334. There too the fuller references to the works of the authors mentioned in the last column of Table I.

TABLE I

	Body weight (grammes)	Nerve cell		Reference to authors, date and page of reported measurements
		Mean diameter (Micra)	Des- cription	
1. <i>Elephas indicus</i>	3600000	84.4	Col. ant.	I. Hardesty. (1902). 160, 161
2. <i>Equus caballus</i>	562500	61.9	" "	" " " " "
3. <i>Homo sapiens</i>	72000	58.0	" "	" " " 159, 160
4. <i>Lepus cuniculus dom. A.</i>	2000	39.2	" "	" " " 160
5. <i>Mus norvegicus albinus. A</i>	250	34.7	" "	" " " "
6. <i>Mus musculus albinus</i>	20	27.4	" "	" " " 160, 164
7. <i>Lepus cuniculus dom. B</i>	2000	56.0	Spin.	G. Levi. (1908). 200
8. <i>Mus musculus. A</i>	20	37.2	"	" " " "
9. <i>Canis familiaris. A</i>	23000	80.8	"	" " (1906). 331, 332
10. <i>Canis familiaris. B</i>	3750	67.5	"	" " " " "
11. <i>Mus norvegicus albinus. B</i>	250	16.5	Purk.	Addison. (1911). 469
12. <i>Mus musculus. B</i>	20	13.0	"	Obersteiner. (1913). 5
13. <i>Felis leo</i>	119500	69.5 max.	Betz	Brodmann. (1909). 83
14. <i>Felis pardalis</i>	10433	66.5 med.	"	Bevan Lewis. (1880). 53
15. <i>Felis domestica</i>	3300	69.0 max.	"	Brodman (Lewis) (1909). 83
		60.0 med.	"	Bevan Lewis. (1880). 85

the exponent holding from species to species, as it expresses the relative individual growth of the brain to the adult state.

In consequence of this difference in the fixed relations of the weights of the brain and the body, between homoneuric species on one side, individuals of a species on the other side, i. e. the difference between the phylogenetic and the ontogenetic exponent, small individuals have comparatively more, large individuals comparatively less brain than species of corresponding mean body weight.

This appears graphically in Figures 2 and 3. The difference can become very great in dwarfs and giants of one species; it is very striking in the Figures 5 and 6, which give the accurate outlines, in natural size, of the skull of a medium sized fennec (*Canis zerda*), the smallest species of the genus *Canis*, and one of the smallest individuals of the species Domestic Dog, of a diminutive breed,

TABLE II

Calculated Values of the Exponent r for the Increase of the Volume
of the Nerve Cells with the Body Weight

	Nerve cell Description	Proportion of the body weight	Exponent
1. <i>Elephas indicus</i> and <i>Mus musculus albinus</i>	Col. ant.	180000 : 1	0.2789
2. <i>Equus caballus</i> and <i>Mus musculus albinus</i>	" "	28125 : 1	0.2387
3. <i>Homo sapiens</i> and <i>Mus musculus albinus</i>	" "	3600 : 1	0.2747
4. <i>Lepus cuniculus dom.</i> A and <i>Mus musculus albinus</i>	" "	100 : 1	0.2333
5. <i>Mus norvegicus albinus.</i> A and <i>Mus musculus albinus</i>	" "	12.5 : 1	0.2805
6. <i>Lepus cuniculus dom.</i> B and <i>Mus musculus.</i> A	Spin.	100 : 1	0.2665
7. <i>Canis familiaris.</i> A and <i>Canis familiaris.</i> B	"	6 : 1	0.2975
8. <i>Mus norvegicus albinus.</i> B and <i>Mus musculus.</i> B	Purk.	12.5 : 1	0.2832
9. <i>Felis leo</i> and <i>Felis domestica</i>	Betz	36 : 1	0.2804
10. <i>Felis pardalis</i> and <i>Felis domestica</i>	"	3 : 1	0.2681

probably a toy-terrier, of the same body weight, after photographs which I owe to Prof. W. LECHE at Stockholm. The brain weight in the diminutive individual of Domestic Dog, with only a ninth of the mean body weight of the species, is indeed quite 87% more than the mean of the smallest species of Canidae¹⁾. The amount and the plus or minus sense of this difference with species is dependent on their body weight. The smaller the species of the genus *Canis*, the more it is exceeded in brain weight by an individual of the same size of the Domestic Dog species. Domestic dogs of the size (the body weight) of the common (Euro-

¹⁾ The body weight of a female fennec, killed in its African home, was 1.5 kg. according to KLATT (Studien zum Domestikationsproblem, p. 36), the weight of the brain was 25.2 g. The capacity of an almost adult female skull in the Leiden Museum of Natural History, observed by me, was 20 c.c., of two other skulls, of which the sex is not indicated, in the Berlin Zoological Museum, the capacity observed by KLATT, is resp. 20 and 18 c.c. When for the species 2 kg. body weight, and 27.9 gr. brain weight is assumed, this gives certainly about the true ratio; absolutely these weights are possibly estimated too high. From the observations of KLATT (Ibid., Haupttabelle) on 17 adult toy-terriers (Zwergpinscher), of an average body weight of 3.11 kg., with 58.1 gr. brain weight, I calculate for 2 kg. body weight of this diminutive breed the brain weight at 52.3 gr.

pean) Fox have only slightly more than **28 %** more brain weight than this small species. Very large domestic dogs, of about 40 kg.,

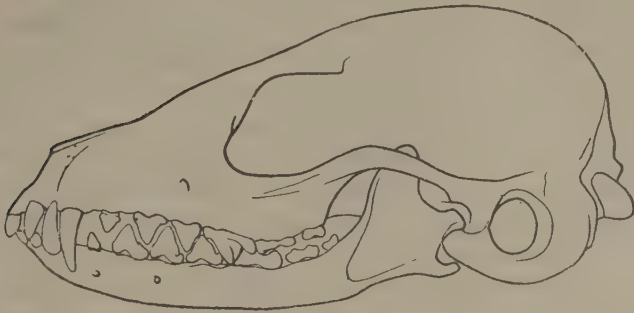


Fig. 5.

Skull of a fennec (*Canis zerda*), in natural size.



Fig. 6. Skull of a domestic dog of diminutive breed, in natural size.

i.e. the mean body weight of the Wolf, have **25 %** less brain weight than this largest member of the Canidae¹⁾.

It is now of great importance that the ontogenetic exponent is equal to the exponent indicating the relation of the body weights or

¹⁾ Through comparison with two foxes from France and one wolf from America LAPICQUE (loc.cit. p. 329) had already pointed out these differences in 1907. Afterwards KLATT (Ibid., p. 36) corroborated them with more numerous data through a comparison with the Jackal and the Wolf. According to KLATT's records on ten (German) foxes (Ibid., p. 37) and eleven domestic dogs (Haupt-tabelle) of about the same size, 6.12 kg. may be taken for the body weight of

volumes to the volumes of homologous nerve or ganglion cells, both between adult individuals of one species and between different species. This confirms that, with increasing body weight, from adult individual to adult individual of one and the same species, only the volume of each nerve cell in the brain increases, but from species to species at the same time the number of these cells, and that the number does so in the same ratio as the volume increases, which had already been rendered probable by other facts. Comparison of the brain weight in function of the body weight between the two sexes¹⁾ had led me to the result, on the ground of the measurements of the diameter of the muscle fibres by BOWMAN and by SCHWALBE and MAYEDA, and the observations of muscle weights by THEILE, that the number of muscle fibres of Man is equal to that of Woman. From the comparison of the relative quantity of brain and muscularity of the Europeans and the Japanese it had appeared to me that the relatively larger volume of the brain and of the muscles of the latter finds its explanation, not in the different number of the neurones and the muscle fibres, but in the larger cross-section of the separate muscle fibres, larger separate volume of the nerve cells²⁾. Hence, between Man and Woman, between the Japanese and the European, i. e. within the species of *Homo sapiens*, only the volume, not the number of the nerve cells and of the muscle fibres differ.

the Fox, 52 gr. for its brain weight; the average body weight of the eleven domestic dogs is 6.6 kg., their average brain weight 68 gr. Hence with equal body weight, the latter brain weight is 28.4% more than for the Fox. Comparison of these dogs with the jackals (*Canis aureus*) leads to similar results. The average body weight of fourteen jackals according to KLATT's observations (Haupttabelle) is 6.836 kg., their average brain weight 57.1 gr. The difference with dogs of the same body weight is 20.1 %, somewhat less than the difference of these with the Fox, because the cephalisation of the Jackal is a little higher. In contrast with domestic dogs of the size of these small Canidae, domestic dogs of the size of the Wolf have 24.8 % less brain than averagely this largest species of the genus *Canis*. From KLATT's records (Haupttabelle) of brain weights of six and body weights of four Lapland and Russian wolves, and of cranial capacities of 23 European and American wolves (KLATT. Ueber die Veränderung der Schädelkapazität, p. 166), averagely 161 c.c., I derived a body weight of the species of 40 kg., a brain weight of 147.6 gr. Absolutely both weights may be a little too high, relatively most likely they are about right. Accordingly the Wolf is about equal in its cephalisation with the Fox. But twenty dogs of KLATT's observations, of 30 to 48 kg., averagely 37.6 kg. body weight, have an average brain weight of 109.4 gr.

¹⁾ Under this title in these Proceedings, Vol. XXI, p. 868—869. (1919).

²⁾ Eug. Dubois, On the Significance of the Large Cranial Capacity of *Homo neandertalensis*. These Proceedings, Vol. XXIII, p. 1281. (1921).

From the still little known, but very important measurements of muscle fibres by VON DER MALSBURG¹⁾ the same may be derived for individuals of unequal size of different Mammalia.

In Table III some individuals of five species, being in a fairly good condition, and of a body weight as different as possible, are compared as regards the relation between the latter and the cross-section of homologous muscle fibres. This cross-section appears to increase in direct ratio to the surface of the body, hence to the cross-section of homologous muscles, which means that the number of muscle fibres within a species does not change with increasing size of the body. Also the number of nerve fibres and that of the nerve cells of the brain may then be admitted as being the same within a species.

This is certainly not the case between different species, for when the specific differences of caliber are taken into account, through which homologous muscle fibres of different species of animals (just as not homologous muscles of the same species) are distinguished, not much remains of a direct influence of the size of the body on this caliber of the muscle fibre. The number of the muscle fibres must, therefore, greatly increase with the size of the animal species. According to VON DER MALSBURG the average diameter of the muscle fibres in the rectus abdominis and the gastrocnemius is for the Ox 45.88 micra (in its different breeds 35.35 to 63.37 micra), for the Horse 39.20 micra (breeds 33.26 to 48.60 micra), for the Pig 42 micra, for the Sheep 22.61 micra (breeds from 18.50 to 30.85 micra), for the Goat 18.90 micra. For the average diameter of the muscle fibres in the gastrocnemius of the Dog (calculated from v. d. M.'s records, applied to the mean body weight of this species) 21 micra may be assumed, the average of four hares is 19.20 micra, and of five mice 17.40 micra, the body weights of these two last species being to each other as 200:1.

With not inconsiderable specific differences (but much smaller than between the different breeds and individuals), only small differences between these species are to be ascribed to the influence of the size of the body. Thus also MAYEDA and SCHWALBE²⁾ found in

¹⁾ KAROL VON DER MALSBURG, Die Zellengrösse als Form- und Leistungsfaktor der landwirtschaftlichen Nutztiere. Arbeiten der Deutschen Gesellschaft für Züchtungskunde. Heft 10. 367 pag. Hannover 1911.

²⁾ R. MAYEDA, Ueber die Kaliberverhältnisse der quergestreiften Muskelfasern. Zeitschrift für Biologie. (KÜHNE und VOIT). N.F. Bd. 9, der ganzen Serie Bd. 27, p. 129. München und Leipzig 1890. — G. SCHWALBE und R. MAYEDA, Ueber die Kaliberverhältnisse der quergestreiften Muskelfasern des Menschen. Ibid, p. 487, 489, 515.

TABLE III

Relation of the Cross-Section of Homologous Muscle Fibres to the Body Weight,
in Individuals of Different Sizes of one Species

Page with V. D. MALSBURG	Species	P Body weight, in kg.	^m Diameter of the muscle fibres, in micra		Calculated power of P, which is propor- tional to m^2
			Gastro- cnemius	Mean of Rectus abdominis and Gastro- cnemius	
	Horse				
146	4 heavy, average	712.5		46.16	0.6459
146	2 light "	290		34.53	
102	Belgian male	850		49.60	0.6750
102	Pony, male	300		34.90	
102	5 males, average	740	48.79		0.7218
104	4 " " "	437.5	40.36		
	Ox				
95	4 bulls, average	662.5	45.17		0.6670
97	3 " "	416.6	38.70		
95	Bos taur. primig. var. Sarm.	600	45.00		0.6030
98	" " " " "	350	38.25		
	Pig				
108	Wild, male	130	48.25		0.7800
108	" female	80	40.10		
149	Yorkshire	100		44.00	0.5480
149	" dwarf (much emaciated)	11.8		24.50	
	Dog				
109	Newfoundland (emaciated)	49	38.10		0.7402
109	Fox-Terrier	9	20.35		
	Rabbit				
326	Domestic, large breeds, average	3.3		36.65	0.6946
326	" small " "	1.5		27.87	
				Mean	0.6751

their measurements the muscle fibres in the gastrocnemius of a mouse about as thick as in the homologous muscle of a woman and of a dog (but thinner than in that of a man). In the masseter of their mouse the muscle fibres were about as thick as in the masseter of the man, but less thick than in the dog. That the size of the body from species to species has only little influence on the caliber of the muscle fibres appears also from this that G. LEVI¹⁾ found the diameter of the thickest muscle fibres in the rectus femoris of a mouse not below that in a rat (twenty times as heavy).

It may, therefore, be admitted that in homoneuric species the number of muscle fibres, and then also proportionally that of the ganglion cells in the brain, greatly increases with the size of the body. But the available data do not enable us to calculate the exact relation of the body weight to the number of the muscle fibres in these species. On the ground, however, on one side of the relation found for the brain weight E to the body weight P , according to which E increases proportionally to $P^{6/10}$ between homoneuric species, and proportionally to $P^{6/18}$ between adult individuals of the same species, and on the other side, on the ground of the relation found for the volume of the separate nerve cells C to the body weight, according to which C increases in the ratio of $P^{6/18}$, both between individuals and between species; further on the ground of the established fact that between large and small individuals the number of the muscle fibres, hence proportionally that of the nerve cells in the brain, does not differ, but that it differs greatly between large and small species, we may conclude, that also the number of the nerve cells between homoneuric species increases in the ratio of $P^{6/18}$.

The difference between the phylogenetic and the ontogenetic exponent is thus rationally explained. It means that in the origination of the species, increase of the size of the body is accompanied with multiplication of the nerve cells, through cell division (in non-homoneuric species this multiplication is greater in certain parts of the brain)²⁾. With the establishment of larger adult individuals

¹⁾ GIUSEPPE LEVI, Studi sulla grandezza delle cellule. Archivio di Anatomia e di Embriologia. Vol. V, p. 327. Firenze 1906.

²⁾ Direct counting of the cells in the grey cortex of Monkeys by OTTO MAYER (Mikrometrische Untersuchungen über die Zelldichtigkeit der Grosshirnrinde bei den Affen, Journal für Psychologie und Neurologie, Bd. 19, p. 237. Leipzig 1912) teaches that per m.m.², calculated throughout the cortex, only about the same number of cells occur in the small Hapale (3448) as in the larger Chrysothrix (3603) and in the still larger Cebus (3581). As the brain weights in these heteroneuric and from the smallest to the largest species higher cephalized American

of a species, there is no nerve cell division; these cells only increase in volume, which they also do with the origination of larger species. For this increase of the nerve cell volume is a mechanical necessity, as may appear further below.

That phylogenetic increase of the volume of the brain is actually brought about by cell division, associated with equivalent increase of the separate cell volume, is also proved by the fact that in related, but heteroneuric species, with equal body weight, the volumes (or weights) of the brain or — what comes to the same — with unequal body weight, the calculated coefficients of cephalisation, in many cases, are to each other as 1, 2, 3, 4. The cranial capacities of the Chimpanzee (450 c.c.), of *Pithecanthropus* (900 c.c.), and of the male Australian aboriginal (1350 c.c.) are to each other as the numbers 1 : 2 : 3. The coefficient of cephalisation of the Man-like Apes is twice that of the Old World Monkeys and Baboons; *Cebus* has double the cephalisation coefficient of *Chrysotrrix*; in the *Megachiroptera* it is twice that of the *Microchiroptera*. The coefficient of the Tree Shrew (*Tupaja*) is four times that of the Common Shrew (*Sorex*) and the Musk Shrew (*Crocidura*). The coefficients of the genera *Mus*, *Lepus*, and *Sciurus* are to each other as 1 : 2 : 3. The genera *Tapir*, *Sus*, and *Hippopotamus* have a coefficient of cephalisation half as great as that of the Horses, the Deer, the Giraffe, the Antilopes, and the Oxen. The Chevrotain (*Tragulus*) also has a coefficient only half so great as the modern-type Ruminants. It is extremely interesting that among the *Mustelidae*, the Polecat (*Putorius putorius*), the Stoat (*Putorius ermineus*), and the Weasel (*Putorius nivalis*) possess a coefficient of cephalisation only half so great as the Beech-Marten (*Mustela foina*) and the Pine-Marten (*Mustela martes*). In this respect the Badger (*Meles*) agrees with the former, the Otter (*Lutra*) with the latter group.

We meet here with an important phenomenon, analogous to the "parameter-law" of crystals, and, undoubtedly, intimately connected with the polyploidy of nuclei and consequent rational increase of cell volume.

It may, further, be pointed out that most of the heteroneuric species mentioned with low cephalisation, are small, in comparison with the allied species with high cephalisation. This proves that the phylogenetic growth of the brain, in which — different from what

Monkeys are to each other as 8:24:70, the absolute number of cells increases considerably more than would correspond with the same size of body of homoneuric species. In the nearly homoneuric Gibbon (*Siamang*) and Chimpanzee those numbers are 3160 and 1765, and the brain weights to each other as about 1:3.

is found in the establishment of a new homoneuric species — certain parts of this organ increase to a greater degree than the other parts, and accordingly a heteroneuric species originates, is probably always too accompanied with increase of the bulk of the body. Only with the same increase of the bulk of the body, the increase of the volume of the brain is comparatively greater than in the establishment of a new homoneuric species.

Another peculiarity of the Polecat may be considered in connection with what has been said about its lower cephalisation. When with the observations of weight of the body and the brain by BETHCKE¹⁾ of ten certainly adult polecats, the ontogenetic exponent is calculated, from the five with body weights above 1000 gr. (average 1281.5 gr.) and the five under 1000 gr. (average 769 gr.), **0.42** is found for it, the same value as is obtained from the weights of a very large polecat (of 1700 gr.), from the observations of LAPICQUE²⁾, and a very small one (of 593 gr.), of my own observations³⁾, both adult animals. This exponent is exactly halfway between $\frac{5}{18}$ and $\frac{5}{9}$. In a graph the direction of the ontogenetic line of the Polecat would be seen to deviate from other ontogenetic lines, and approach to coincidence with the phylogenetic line of the genus *Putorius*. Evidently the species of Polecat is in a state of disintegration. Probably the other *Putorius* species are too. Well-known is, indeed, the great variability of all the species of this genus.

In the ontogenetic growth there is an important difference between the nerve cells and the other cells of the body. It is the great merit of GIUSEPPE LEVI and of EDWIN CONKLIN to have pointed this out. In 1906 LEVI⁴⁾ proved for a great number of Mammalia and in 1908 for the Vertebrates in general⁵⁾, that in contrast with most cells, except probably the muscle fibres (and those of the crystalline lens), the size of the nerve cell increases with the size of the animal⁶⁾. The other cells increase in number, not separately in size.

¹⁾ Loc. cit., p. 613.

²⁾ Comptes rendus. Académie des Sciences. (2), Tome 151, p. 1393. Paris 1912.

³⁾ Verhandeling of 1897, p. 36. Also: Bulletins de la Société d'Anthropologie de Paris, 1897, p. 371.

⁴⁾ Loc. cit.

⁵⁾ GIUSEPPE LEVI, I Gangli cerebrospinali. Supplementa al Vol. VII dell' "Archivio Italiano di Anatomia e di Embriologia". Firenze 1908.

⁶⁾ IRVING HARDESTY, already in 1902, found that the size of the motor nerve cells from the spinal chord of various Mammals increases with the size of the body. (Observations on the Medulla spinalis of the Elephant with some Comparative Studies of the Intumescencia Cervicalis and the Neurones of the Columna Anterior. Journal of Comparative Neurology. Vol. XII, p. 125 seq. Philadelphia 1902).

In 1912 CONKLIN¹⁾ showed for different species and individuals of one species of Boat Shell (*Crepidula*), that in spite of the very great differences in body size, "the size of tissue cells is approximately the same in all species examined, and in all individuals of both sexes and of very different sizes. In the main, differences in body size are due to differences in the number of cells present, and not to variations in the size of individual cells. Ganglion cells and muscle cells form the principal exception to this rule". (According to his measurements the diameter of muscle fibres is not greater in the larger species, and only a little greater in large-sized individuals of one species). From his measurements of a gigantic female and a medium-sized male individual of *Crepidula plana* I find for the exponent of relation of the volume of the body and the volume of the ganglion cells the value of 0.3149, which is sufficiently near $\frac{5}{18}$ to prove the existence of the same ontogenetic relation also in the Invertebrates.

As was already mentioned, LEVI is less certain in his conclusion about the muscle fibres; he generally finds them thicker in large animals than in small ones, but the thickness changes much less than the length, and there are many exceptions to the rule. This uncertainty is, indeed, explicable by what was derived above from VON DER MALSBURG's measurements with regard to the larger differences between individuals than between the species.

The nerve cells and the muscle cells are distinguished from most other cells (only the fibres of the crystalline lens make an exception to the general rule) in that early in life — in Man and all Mammalia examined on this point about birth-time — they cease increasing in number through division, but then continue for some time to increase separately in volume. The other cells go on multiplying by division throughout life. The muscle cells continue increasing their separate volume at least up to the adult state of the individual. But the nerve cells also stop doing this in the early youth of the individual.

A consequence of this peculiarity of the nerve cells is, that early in the life of the individual the brain assumes the volume of the adult state of the body; in a male child for instance, at the age of nine, in a female child when six years old. But a similar remark holds among others for the Dog, the Rat, the Great Ant-Eater, the Sparrow, the Chicken, the Crocodile, the Frog, the Salmon,

¹⁾ EDWIN G. CONKLIN, Body Size and Cell Size. *Journal of Morphology*. Vol. 23, p. 159—188. Philadelphia 1912.

in short for all the Vertebrata, and also for the Invertebrata. At birth the brain weight of Man is $\frac{1}{9}$, and in the adult state of the body $\frac{1}{47}$ of the body weight. At its birth a dachshund has $\frac{1}{29}$, and in the adult state $\frac{1}{135}$ of its weight in brains. With a body weight of 7 grams the Brown Rat has less than $\frac{1}{10}$, and when it is full grown $\frac{1}{160}$ of its weight in brains. In the Bull Frog of $4\frac{1}{2}$ grams of body weight, the brain weight constitutes $\frac{1}{100}$ of it, and when the body weight has increased to 200 grams, the ratio of the brain weight is only $\frac{1}{1000}$. This gives the skulls, of them all in their first youth, a much more humanlike appearance than they have in the adult state. The great resemblance of the skull of young Apes with that of Man cannot, therefore, have the special significance that is sometimes ascribed to it.

The peculiarity of the nerve cells manifested in this early cessation of cell division in the ontogenetic growth, now accounts also for the long interruptions in the phylogenetic growth, (also resting on cell division), especially if this growth is stronger in certain parts of the brain and mostly in those with the highest integrative action. This phylogenetic growth then takes place with long intervals, as shown anatomically in the brain quantities of allied heteroneuric species of the present animal world, paleontologically by comparison of animal forms of the present time with those of a former world order.

But why are the nerve cells distinguished in this conspicuous way from all other cells, with the exception of the muscle cells, which act under their influence? We find the volume of the nerve cells to be in a particular, in what precedes not yet causally explained relation to the body weight. What is the meaning of that "strange" $\frac{5}{18}$ power? To a proportionality with the $\frac{6}{18}$ or $\frac{1}{3}$ power of the body weight, i.e. with the linear dimension of the body, we could readily ascribe a dynamic significance; as the mass of the body increases as P , the physiological cross-sections of the muscles, which determine the muscular force, the sensual areas, the areas that determine metabolism increase only proportional to $P^{\frac{2}{3}}$, it would be comprehensible if this inadequacy implied an increase of the volume of the nerve cell proportional to $P^{\frac{1}{3}}$. But this takes place in a definite, smaller proportion, according to $P^{\frac{5}{18}}$.

In order to detect the meaning of this latter proportionality I examined on a former occasion ¹⁾ in what relation the volumes of the principal constituents of the nerve cell, the nucleus and the plasma, are to each other and to the body weight. The result of this examination is recorded in Table IV.

¹⁾ These Proceedings, Vol. XXII, p. 671—675. (1920).

TABLE IV

Calculated values of the exponents d , $\lambda (= \frac{5}{18} d)$ and k for the increase of the plasma volume D with the cell volume C and with the body weight P , and of the nucleus volume K with the cell volume C . (From measurements of the diameters of ganglion cells and their nuclei by GIUSEPPE LEVI, and corresponding linear dimensions of their plasma).¹⁾

Species	Situation of the ganglion cells	d in $(\frac{C}{C_1})^d = \frac{D}{D_1}$	λ in $(\frac{P}{P_1})^\lambda = \frac{D}{D_1}$	k in $(\frac{C}{C_1})^k = \frac{K}{K_1}$
1. <i>Bos taurus</i> , 1 and <i>Mus musculus</i> , 8	Gangl. spin.	1.198	0.3327	0.5348
2. <i>Bos taurus</i> , 2 and <i>Mus musculus</i> , 8	id. id.	1.203	0.3342	0.5268
3. <i>Lepus cuniculus</i> , 4 and <i>Mus norvegicus</i> , 7	id. id.	1.202	0.3338	0.5987
4. <i>Lepus cuniculus</i> , 4 and <i>Mus musculus</i> , 8	id. id.	1.206	0.3351	0.6143
5. <i>Mus norvegicus</i> , 7 and <i>Mus musculus</i> , 8	id. id.	1.210	0.3362	0.6288
6. <i>Cavia cobaia</i> , 5 and <i>Arvicola arvalis</i> , 9	id. id.	1.216	0.3378	0.6703
7. <i>Cavia cobaia</i> , 6 and <i>Arvicola arvalis</i> , 9	id. id.	1.259	0.3497	0.6025
8. <i>Felis domestica</i> , 10 and 11, gln. cerv. V and cocc. I	id. id.	1.123	0.3119	0.6466
9. <i>Python</i> (species), 12 and <i>Seps chalcides</i> , 14	id. id.	1.187	0.3296	0.5892
10. <i>Varanus arenarius</i> , 13 and <i>Seps chalcides</i> , 14	id. id.	1.203	0.3341	0.5386
11. <i>Bos taurus</i> , 15 and <i>Mus musculus</i> , 16	Rad. ant. spin.	1.195	0.3320	0.6555
12. <i>Canis familiaris</i> , 17 and <i>Canis vulpes</i> , 18	Purkinje cerebell.	1.199	0.3330	0.6651
13. <i>Canis familiaris</i> , 21 and <i>Putorius putorius</i> , 22	Gangl. cerv. sup. n. sympath.	1.248	0.3466	0.6523
Mean		1.204	0.3344	0.6095

The cells compared there are all adult, and homologous as regards their general character, but not being in each case of accurately corresponding places in the central nervous system, they cannot be directly referred to the body weights.

¹⁾ Cf. in these Proceedings, Vol. XXIII, p. 672, Table I. There on p. 674 also the above calculations were already published in Table II.

When now the power of the cell volume C , is calculated, by which the plasma volume D increases, we find for it 1.2 or $6/5$. We find 0.6 or $3/5$ for the power of the cell volume by which the nucleus volume K increases proportionally. On increase of the nerve cell the plasma volume varies, therefore, proportionally as the square of the nucleus volume. As $6/5 \times 5/18 = 6/18$ or $1/3$, the plasma volume appears to increase proportional to the third root of the body weight or $P^{1/3}$, and the nucleus volume proportional to the sixth root of the body weight or $P^{1/6}$.

Thus it appears that only the plasma, which is directly connected with the nerve fibre, in such a way that the axis cylinder passes into it, has the said direct dynamic significance. The nucleus, which is always separated from the plasma by a membrane, is directly concerned only with the life of the cell and its intern mechanism. The nucleus, in the common opinion, is the bearer of the hereditary properties in the nervous system, and it regulates the constructive metabolism, growth, and reproduction of the cell.

But still this "strange" exponent $5/18$ is only partly accounted for. Why does the volume of the nucleus K vary proportional to the sixth root of the body weight, i. e. to the square root of the body length, \sqrt{L} , or K^2 to L ?

This too I already discussed on that former occasion. The following remarks may now be added.

It has appeared chiefly from the then cited cytological researches and studies by GERASSIMOW, BOVERI and R. HERTWIG that the volume of the plasma depends on that of the nucleus: The relative size of the nucleus is determined by a dynamic state of equilibrium between the volume of the nuclear substance and the free surface of the cell, i. e. of the plasma. Further that with such a constant ratio the rate of cell division also remains constant. Now we actually see in the largest, i. e. full-grown homologous ganglion cells, in every case compared above, the volume of the nuclear substance increase in nearly quite the same relation with the body weight as the free surface of the cell, for $P^{1/6} = P^{9/54}$ and $P^{5/18} \times 2/3 = P^{10/54}$. It may, therefore, be admitted that these cells are in such a dynamic state of equilibrium. The volume of the nucleus increases, indeed, somewhat less than exactly proportional with the surface of the cell (which would be required for cell division), but in this condition of the cell it remains in equilibrium with the general dynamic condition of the body. For the metabolism of the cytoplasm increases in the same rate with the increasing volume of the nuclear substance K , and consequently the kinetic energy issuing from the nucleus proportionally to K^2 .

But we found also K^2 increasing proportionally to L or $P^{1/3}$. And this is the same ratio as exists between the mass of the body and the muscular force, the metabolism, the rate of conduction of the nerve impulses.

It has been found cytologically that with constant relation of nucleus and plasma also the rate of cell division remains constant. And already in 1895 ALEXANDER SUTHERLAND¹⁾ had shown that the time of incubation of bird species and the time of gestation of related species of mammals increases proportional to $P^{1/6}$ or $\sqrt[6]{L}$; weight and length being those of the full-grown animal's body.

In general this time is $T = n\sqrt[6]{P}$, in which n is a constant, almost the same for all bird species, but different for every order or family of the Mammalia, which tends to increase with the increase of "nerve complexity, as gauged by size and efficiency of brain". Its amount is in indubitable connection with that of the coefficient of cephalisation α , which is determined by the heteroneuric increase of the number of nerve cells; but n certainly increases less greatly and is, in Mammalia, also dependent on other circumstances (as the non-coincidence of the dates of copulation and fecundation). The values n and α are highest in Man, Apes, and the Elephant. The 105 bird species mentioned by SUTHERLAND differ relatively little inter se in their cephalisation, but in some its influence on the time of incubation can yet be recognized, such in the Owls in comparison with the Gallinae. Thus the time of growth, determined by cell division, to birth appears to be in the same relation to the body weight of the adult animals as the nucleus volume of full-grown homologous nerve cells, which cease dividing at birth. This means equal increase of the number of nerve cells to their separate volume. Again, finished cell division in the brain implying completion of linkage in the nervous integrative machinery, it thereby causes mechanically birth, of mammal as well as bird.

In the origination of a heteroneuric species the phylogenetic growth of the brain volume is not uniform, in simple mechanical accordance with the phylogenetic growth of the body, as in the establishment of a larger homoneuric species, but it is stronger in those most compounded parts of the brain, where new chains of cells are superposed upon the preëxisting chains, superiorly integrating

¹⁾ ALEXANDER SUTHERLAND, Some Quantitative Laws of Incubation and Gestation. Proceedings of the Royal Society of Victoria. Vol. VII. (New Series), p. 270—286. Melbourne 1895. Also in The Origin and Growth of the Moral Instinct, p. 69—71 and 101—102. London 1898.

parts upon the inferiorly integrating parts of the brain. Yet the brain volumes, corresponding to equal body weights, of heteroneuric species are to each other as 1 to 2, 3 or 4, which implies that the volume of those superposed chains of cells, in the origination of a heteroneuric species, is equal to, double or triple the volume of the preëxisting chains. We may infer from this, that the phylogenetic progress of the brain, by evident discontinuous variation (mutation), after all depends on segregation of aliquot parts from polyploidly increased nuclear substance.

As, again, the size of the nerve cell body and its chief component parts is adjusted to the mechanism of the whole animal, and every nerve cell is bound to coöperation with many homologous, and non-homologous nerve cells, its relatively stable character, manifested in the ontogenetically limited, and phylogenetically infrequently, but then from the beginning definitely increased multiplication by division, becomes comprehensible, especially when — in the origination of a heteroneuric species — the multiplication must be greater in the most compounded and intricately functioning parts of the brain.

Physiology. "*A further Contribution concerning the function of the Otolithic Apparatus.*" By Prof. R. MAGNUS and A. DE KLEYN.

(Communicated at the meeting of May 27, 1922).

In a previous publication ¹⁾ we demonstrated that when caviae are centrifuged by WITTMACK'S method, being thereby deprived of otolithic membranes, the labyrinth-reflexes *resulting from position* (tonic labyrinth-reflexes on the extremities, "Labyrinth stell-reflexes", and compensatory eye-positions) will disappear, but that, on the other hand, the labyrinth-reflexes *responding to movement* (rotatory actions and after-reactions on head and eyes and the reflexes on progression-movements) will persist. It follows that the above position labyrinth-reflexes are otolithic reflexes, since change of position of the head in space does not enable us to elicit a *change* of the stimulation in the sensory epithelium of the otolithic maculae, but does not at all mean that the sensory epithelium cannot, under these circumstances, be in a permanent condition of stimulation. It is *a priori* quite possible that the sensory epithelium of the maculae, like that of the retina, continually produces stimuli, whose magnitude, in the absence of the removed otolithic membranes, can no more be altered by the changes of position of the head in space.

This conception was brought home to us by experiments to be published afterwards.

In order to go further into this subject we started from the following consideration:

The extirpation of *one* labyrinth in a normal animal brings about an intricate complex of phenomena. A previous minute inquiry ²⁾ into these phenomena enabled us to establish the following symptoms as resulting directly from the unilateral extirpation of the otoliths (membranes + sensory epithelium) or rather from the activity of the otolithic organs on one side only:

- a. Rotation and flexion of the head towards the missing labyrinth.
- b. Eye-deviation: the eye on the side of the removed labyrinth, deviating downwards, the other upwards..

¹⁾ These Proceedings, Vol. XXIII, p. 907.

²⁾ Pflügers Archiv. 154. 178. (1913).

As secondary results from the rotation of the head sub α appear change of posture of the whole body, difference of tonus in the extremities, rolling movements etc.

We do not know as yet which part of the labyrinth is responsible for a transitory difference of tonus in the extremities, which persists also with the head in the normal position towards the trunk. This symptom has, therefore, to be left out of consideration in the following discussion.

On the basis of these findings we performed the following experiments:

Caviae were centrifuged after the familiar method of WITTMACK. Now only those animals were used for further experimentation in which clinically all labyrinth-reflexes of position disappeared and all movement-reflexes maintained themselves, or, in other words, animals in which it could be expected that all the otoliths had been completely detached on either side.

In order to eliminate as much as possible a stimulating, or paralyzing influence of the removal itself on the sensory epithelium, the animals were regularly examined and the experiment proper was started only from 7 to 9 days after the centrifugation.

In this procedure about 0.1 cc. of a 5% cocaine solution was injected unilaterally through the ear-drum into the middle-ear, in order to paralyse the whole labyrinth on that side.

If it should now appear that, after the removal of the otoliths, the sensory epithelium of the maculae was not in a condition of stimulation, it could be expected that no phenomena should reveal themselves after the cocaine injection, with the exception only of a nystagmus consequent on the elimination of the *semicircular canals* on the injected side.

If, however, there is indeed, after the removal of the otoliths a stimulation in the sensory epithelium of the maculae, we may look for asymmetrical phenomena after the cocaine-injection, since at the injected side the sensory epithelium is completely paralysed and there is a constant condition of stimulation at the other side.

After the cocaine-injection a rotation of the head towards the injected side ("Grunddrehung"; utricle) and an eye-deviation (eye at the injected side down, the other eye upwards; sacculus) may then be expected, i. e. phenomena agreeing with those appearing in *normal* animals, if ipsilaterally the labyrinth is paralysed through extirpation or through injection. With this difference, however, that the phenomena in animals with removed otoliths do not vary, as is the case in normal animals after unilateral extirpation of the

labyrinth, with the various positions of the head in space consequent on the varying influence of the otoliths of the unimpaired side, but that these phenomena are constantly the same whatever the position of the head of the animal under examination may be, when it is held up freely in the air.

Five similar experiments were made, which are instanced in the following three protocols:

Cavia R:

- 28/6 1921: All labyrinth-reflexes normal.
Centrifugation: head up, chest inward, time 2 minutes, rate 1000 m. per minute.
- 2/7 1921: Total lack of tonic reflexes.
- 4/7 1921: Reflexes of the semi-circular canal: rotation-reactions towards the right positive, to the left weak.
Progression-reactions: doubtful or lacking.
Total lack of tonic reflexes.
- 5/7 1921: Reflexes of the semi-circular canal (also progression-reactions) all present and symmetrical.
Tonic reflexes: all present. Sits symmetrically, no eye-deviations. In dorsal position with head in normal position to the trunk: no distinct difference of tonus in the extremities.
- 11^h 39'. 0.1 cc of 5% cocaine solution into *left* middle-ear.
- 11^h 41'. Held up in the air with head down: head 90° towards the right. When sitting OD¹⁾ down OS²⁾ up (consequently stimulation of the left labyrinth).
- 11^h 43'. Head down: head symmetrical again.
- 11^h 47'. Head down: head 20—30° rotation to the left, slightly turned to the left. When sitting a slight levoersion of the head, no distinct eye-deviations.
- 11^h 49'. Head down, 45° levo-rotation. When sitting falls on the left side. Head in normal position: no distinct difference of tonus in the extremities. If moved on the ground to the right much greater resistance than against moving to the left, strong inclination to the left (incipient paralysis of the left labyrinth).
- 11^h 51'. Head down: 70° levo-rotation. When sitting head-nystagmus towards the right. Is moved on the ground: rolling to the left. No distinct eye-deviation.
- 11^h 54'. Head down 90° levo-rotation. OS slightly downwards. OD upwards.
- 12^h. OS weak nystagmus beats anteriorly upwards. OD posteriorly downwards. No change of the phenomena with a change of the position of the head in space.
- 12^h 3'. Marked spontaneous nystagmus, direction as at 12^h.
- 12^h 6'. Marked deviation and nystagmus, do not change with a different position of the head in space.

¹⁾ OD means Right eyeball.

²⁾ OS means Left eyeball.

- 6/7 1921: Reflexes of the semicircular canal: all present and symmetrical.
 Tonic reflexes: all absent, asymmetry of cocain-test quite disappeared.
 12^h. Decerebration, fair stiffness.
 Shifting from ventral to dorsal position: no trace of tonic labyrinth-reflexes. Rotation of the head in lateral position: Typical cervical reflexes, no labyrinth-reflexes.

Cavia S.

- 28/6 1921: All labyrinth reflexes present and normal.
 Centrifugation: head up, chest inward, time 2 minutes, rate 1000 m. per minute.
- 4/7 1921: Reflexes of semicircular canal: asymmetric reflexes. Rotation-reactions on head and eyes with rotation to the right weak, with rotation to the left strong.
 Progression-reactions: weak; extension of the legs even lacking.
 Tonic reflexes: lacking, only slight „Grunddrehung” to the left.
- 7/7 1921: Reflexes of semicircular canal: present and symmetrical. Progression-reactions weak but present.
 Tonic reflexes: lacking, no more „Grunddrehung”. Sits symmetrically. No eye-deviation.
 Dorsal position head in normal position towards the trunk; no difference of tonus in the extremities.
- Injection of cocain in the *left* middle-ear.
- 12^h 30'. Held up in the air, head down: dextro-rotation of head (stimulation of the left labyrinth).
- 12^h 30¹/₂'. Head down: head, in normal position, not turned.
- 12^h 31'. Head down: levo-rotation of the head (incipient paralysis of left labyrinth).
- 12^h 31¹/₂'. Head down: 60° levo-rotation of the head.
- 12^h 33'. When sitting, head turned and flexed to the left: clock-hand movements to the left, no nystagmus.
- 12^h 34'. OS downward, OD upward; no nystagmus.
- 12^h 34¹/₂'. Marked eye-deviation, no nystagmus: no difference of deviation with change of position of head in space. Head down: head turned 90° to the left.
- 12^h 36'. Right lateral position: head in position of normal sitting animal.
 Left lateral position: head in dorsal position.
 Dorsal position: head right lateral pos.
 Head up: head left lateral position. } No change of the rotation of the head with different position of the head in space.
- 12^h 38'. No nystagmus.
- 12^h 40'. Rotation to the right and to the left: eye-rotation reaction and nystagmus.
 “ “ “ “ “ “ : head rotation reaction positive.
- On the ground: clock-hand-movements to the left; pushed with experimenter's foot: rolling once to the left.
- 12^h 52'. Evident eye-deviation: for the first time very strong spontaneous nystagmus, OS anteriorly upward, OD posteriorly downward.

- 4h. When sitting, head flexed and with maximum rotation to the left, marked rolling movements, strong spontaneous nystagmus.
- 8/7 1921: Tonic reflex entirely lacking. Yesterday's asymmetry quite disappeared.
- 9/7 1921: Animal dyspnoeic. Decerebrate rigidity not good.
Tonic labyrinth reflexes decidedly not present.

Cavia F.

- 28/5 1921: All labyrinth-reflexes positive.
Centrifuged with head up, chest inward, time 2 minutes, rate 1000 m. per minute.
- 31/5 1921: Semicircular canal reflexes: Rotation-reactions and after-reactions: positive.
Progression-reactions: lift-reaction positive, the others weak.
Tonic reflexes: lacking.
- 2/6 1921: Reflexes of semicircular canal: all positive. Tonic reflexes: lacking.
- 5h 12'. 0,05 cc. 10% cocain through left tympanum.
- 6 hour. Sitting with head placed in the normal position: OD upward, OS downward (incipient paralysis of left labyrinth).
- 6h 2'. Sitting with head turned a little towards the left, the whole animal inclines to the left.
Hanging with head down: "Grunddrehung" 90° to the left.
- 6h 6'. Rotating with head *inward*, rotating to the left, weak rotation-reaction of the head, distinct after-reaction. Dextro-rotation: marked rotation-reaction of the head and no after-reaction.
- 6h 7'. Eye-rotation reactions: dextro rotation, distinct reaction with nystagmus, no after-reaction. With levo-rotation: reaction and afterreaction.
- 6h 10'. Progression-reaction: Liftreaction not distinct.
"Springing reflex" positive.
Muscular tremor: positive in all directions except posteriorly.
Tonic labyrinth-reflexes negative.
Position of the head in the air with:
- | | | |
|---|---|--|
| <p>Right lateral position: head in normal position to the trunk through "Grunddrehung", often hangs down.</p> <p>Left lateral position: head in dorsal position through "Grunddrehung".</p> <p>Head up: head in left lateral position, animal now becomes restless (cocain-action).</p> <p>Head down: head turns 90° to the left.</p> <p>Dorsal position: head in right lateral position through levorotation, often also in dorsal position with left flexion.</p> | } | <p>Ergo constant rotation of the head, which does not change with change of position of the head in space.</p> |
|---|---|--|
- 6h 18'. When sitting with head placed in the normal position: OD anteriorly upward, OS posteriorly downward. Nystagmus just the opposite way.
- 6h 33'. Right lateral position: OS posteriorly downward, nystagmus the opposite way. Eye-deviation and nystagmus of the left eye are the same with right and left lateral position of the head and equally strong; the same holds good also for OD.

- 7/6 1921: Animal sits symmetrically, no eye-deviation. .
 Reactions of semicircular canal: all positive.
 Tonic reflexes: all lacking. Asymmetrical phenomena quite gone as in cocain-test.
- 8/6 1921: Like previous day. When sitting, head sometimes turned very slightly to the right, for the rest animal sits symmetrically, no eye-deviations.

Anatomical examination by Dr. M. DE BURLET. All otolithic membranes detached.

- Right sacculus; sensory epithelium without membrane; the otolithic membrane isolated in the sacculus between ductus endolymphaticus and the back-part of the sensory epithelium.
- Right utricle; sensory epithelium without membrane; the otolithic membrane lies between the posterior portion of the macula and the entrance to the crus commune.
- Left sacculus; sensory epithelium without membrane: the otolithic membrane rests against the lateral wall of the sacculus and above the macula.
- Left utricle: sensory epithelium without membrane; the otolithic membrane is detached towards the inner side and above the macula but lies in the utricle.

These experiments go to show that for more than a week after the removal of the otolithic membranes the sensory epithelium is still in a constant condition of stimulation. When one labyrinth is for some time eliminated by cocain, the stimuli emanating from the non-injected labyrinth will induce asymmetrical phenomena, similar to those after unilateral extirpation of the labyrinth in normal animals, with this difference, however, that in the centrifuged animals injected unilaterally with cocain, these phenomena do not change with a *change* of position of the head in the air.

Considering that there was a week's wait after the centrifugation, it is probable that the above condition of stimulation should no longer be ascribed to centrifugation, and that, therefore, to the sensory epithelium of the maculae the power should be assigned of eliciting stimuli, which, owing to the absence of the otolithic membrane, do not vary much as to strength.

The function of the otolithic membranes, then, consists in altering the intensity of this condition of stimulation of the sensory epithelium. This stimulation will be stronger or weaker according as the membranes pull at the epithelium or press upon it.

Relative to the portion of the sacculus (the main part) innervated by the N. sacularis it has been previously demonstrated that the stimulation decreases with pressure and increases with pulling. This mechanism exists probably also for the utricle and maculae.

It appears that for the division of the sacculus (sacculus corner) innervated by the N. utricularis the relations are more intricate.

Our results may perhaps be conducive to the proper conception of the function of the sensory epithelium of the otolithic maculae.

The above-named property of the otolithic apparatus to elicit continuous stimuli even after the otolithic membranes are detached — as here described — undoubtedly demands attention in the further study of the unilateral affection of these organs.

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Geology. — „*Cuba, The Antilles and the Southern Moluccas.*” By
L. RUTTEN.

(Communicated at the meeting of May 27, 1922).

In 1865 E. SUESS endeavoured to show in which way North-, and South-America are connected geologically ¹⁾. Basing upon the then scant geological literature of the borderlands, he partly adopted the conceptions of some few of the older explorers. He observed that the mountain systems of Western North-America do not directly merge into those of Western South-America, but that in South-Mexico and in Guatemala the coastal ranges bend round, ramifying there in different chains, which cross transversely the narrow Central America, to proceed on their course in the Greater Antilles. All along the row of the Antilles SUESS imagined to observe the traces of a large chain of folded-mountains, which he conceived to extend along the North Coast of South America, as far as the boundary of Venezuela and Columbia to merge there into the Andes. So he considers the Andes of South-America as a continuation of the mountains of Western North America, but looks upon the curving chain of mountains via the Antilles as the connecting link.

In the region of the Antilles SUESS distinguished three zones: an interior zone of small islands all composed of young volcanic rocks with very young coastal limestones and allied formations, extending from Grenada to Saba; a middle zone, in which in many places older, folded rocks emerge, building up the Antillean-Cordillera proper, extending from Trinidad via Barbados as far as Haiti, branching out there in at least two chains, of which the southmost proceeds via Jamaica to Honduras, while the most northern runs via Cuba to Yucatan; lastly an exterior zone, stretching from Barbuda via the Bahama Islands and Florida to Yucatan and which is supposed to be the remainder of the unfolded and disrupted “Vorland” of the Antillean Cordillera.

Already SUESS had pointed to the striking analogy between the row of the Antilles and the Southern Moluccas. A few years later

¹⁾ E. SUESS, *Das Antlitz der Erde*. I. 1885.

this analogy was discussed further by WICHMANN¹⁾ and MARTIN²⁾. In the Southern Moluccas we also distinguish an interior curve of volcanic islands, an intermediate curve, consisting of the remains of folded mountains, and farther to the east the remainder of the almost undisturbed "Vorland".

In many points the hypothesis of SUESS has been corroborated by subsequent researches. K. SAPPER³⁾ has demonstrated that the peculiar curvature and ramification of the tectonical units in Northern Central America, which SUESS only suspected, really exist. W. SIEVERS⁴⁾ has proved it to be probable that the eastern Cordilleras of Columbia split up in the North into different branches, then bend round to the North-east and to the east, and can be traced as far as Trinidad with rather great distinctness. LACROIX⁵⁾ found in young volcanic rocks of Martinique xenoliths of mica-schist, proving thereby that in the subsoil of this island there still must exist old, metamorphic sediments. HÖGBOM has pointed out the remarkable analogy⁶⁾ between the eruptive rocks of the Virgin Isles and those of the Andes of South-America. In the collections of the chemist RICHARD LUDWIG W. SIEVERS has found a young eruptive rock from Alta Vela, a small island south of Haiti, and has proved the possibility that this islet may be the continuation of the volcanic interior curve of the Lesser Antilles⁷⁾. Finally W. BERGT⁸⁾, who arranged the above-named collections petrographically, has shown the occurrence of old schists in Haiti. Lastly DE LA TORRE⁹⁾ discovered in Western Cuba a fauna of Mammammonites and M. SANCHEZ ROIG¹⁰⁾ established that this fauna bears a close resemblance to the jurassic fauna of San Pedro del Gallo in Mexico, which has been treated in such a masterly way by BURCKHARDT¹¹⁾.

On the other hand SUESS's theory has not been universally accepted

¹⁾ G. E. A. WICHMANN, Samml. Geol. Reichsmus. II, 1887, p. 198 sqq.

²⁾ K. MARTIN, Tijdschr. Kon. Ned. Aardr. Gen. VII, 1890, p. 260 sqq.

³⁾ K. SAPPER, Peterm. Geogr. Mitt. Erg. Hefte 127, 1899, 151, 1905; Report 8th Int. Geogr. Congr., held in the Un. States, 1904.

⁴⁾ W. SIEVERS, Peterm. Geogr. Mitt. 1896, p. 125—129.

⁵⁾ A. LACROIX, La Montagne Pelée et ses éruptions, 1904.

⁶⁾ A. HÖGBOM, Bull. Geol. Inst. Upsala, VI, 1905.

⁷⁾ W. SIEVERS, Zeitschr. Ges. für Erdkunde Berlin, 33, 1898.

⁸⁾ W. BERGT, Abhandl. Gesellschaft Isis. Dresden. 1897, p. 61—64.

⁹⁾ C. DE LA TORRE, C.R. Congrès Intern. Géol. XI, Stockholm, 1910, p. 1021—1022.

¹⁰⁾ M. SANCHEZ—ROIG, Boletín especial de la Secretaría de agricultura, comercio y trabajo, Habana, 1920.

¹¹⁾ C. BURCKHARDT, Bolet. Instit. Geológico Mexico, 29, 1912.

in America. The investigations of Americans have negated rather than substantiated SUSS's conceptions in some respects. J. W. SPENCER¹⁾, for instance, came to the conclusion, chiefly after the study of charts and morphological speculations in connection with them, that the Antilles were not the remains of an old cordillera. This researcher maintained that the whole tract of the Caribbean Sea, the Antilles and the Gulf of Mexico constituted an ancient continental region, which ever since the Miocene had executed the most stupendous vertical fluctuations of an amplitude of many thousands of meters. R. T. HILL²⁾, however, who visited many of the Antilles, is by no means inclined to consider most of these islands as other than true oceanic formations and refuses to believe that there is any connection between the northern Antilles and Barbados-Trinidad, the latter being by him assigned to the South-America mainland. In his aversion to the assumption of old-sedimentary cores in the Antilles east of Western Cuba he even goes the length of questioning the results of BERGT (l.c.) who had established the occurrence of old schists in Haiti on the basis of simple petrographic work.

Neither were the long-continued explorations of T. W. VAUGHAN³⁾, who has contributed so largely to the knowledge of the geology of Central America in modern time, based upon the ideas of SUSS, which, as shown above, were of such pregnant significance for many a European explorer.

Particularly the island of Cuba, where since the Spanish-American war a number of American explorers have been working, seemed to have many features not belonging to the other Antilles. The Spanish mining-engineer SALTERAIN already had mistaken a group of sharply folded rocks from the environs of Habana, where fossils had never been found for cretaceous sediments⁴⁾ and the later American⁵⁾ explorers adhered to this view or contended it only

¹⁾ J. W. SPENCER, *Geol. Magazine* (4), I, 1894, p. 448—451; *Bull. Geol. Soc. America* VI, 1895, p. 103—140; *Transactions Canad. Instit.*, V, 1898, p. 359—368, and many other publications.

²⁾ R. T. HILL, *Bull. Museum. Comp. Zoology*, Harvard Coll., 34, 1899, p. 225 sqq.; *Bull. Geol. Soc. America*, XVI, 1905, p. 243—288, and many other publications.

³⁾ T. WAYLAND VAUGHAN, *Bulletin U.S. National Museum*, Washington, 103, 1919; *Contributions to the geology and paleontology of the West Indies*, publ. by the Carnegie Inst. of Washington, 1919, in which older publications are cited in extenso.

⁴⁾ P. SALTERAIN, *Boletín Mapa geológico de España*, VII, 1880.

⁵⁾ R. T. HILL, *Amer. Journal of Science*, (3), 48, 1894, p. 196—212. *Bull. Mus. Compar. Zoology Harvard Univ. Geol. Series II*, 1895, p. 243—288; B. WILLIS, *Index to the stratigraphy of North America*, U.S. Geol. Survey, Profess. Papers, 71, 1912.

reservedly¹⁾. However, the petrographic habitus of this would-be cretaceous formation, made up of white limestones, of soft, white marls and of loose calcareous sandstones, is quite different from all the cretaceous rocks known from the other Antilles, Central America and Northern South-America, so that Cuba seemed to be isolated from the rest in this respect. Another peculiarity of Cuba seemed to be that on the whole the tertiary is not very thick and only feebly folded: HILL²⁾ says that the tertiary is merely a thin veneer overlying the older formations so that its thickness does not excel 1000 feet, and HAYES-VAUGHAN-SPENCER have reproduced profiles of the island in which everywhere a very feebly folded tertiary formation is marked³⁾. If this is correct, Cuba differs very much from the other Antilles, for in Haiti⁴⁾, Barbados as well as in Trinidad⁵⁾ there are very thick and intensely folded tertiary deposits, as may be expected in a young mountain-range, such as SUESS asserts the Antilles to be composed of.

A two months' stay in Cuba, in the months of March and August of the past year, put me in a position to explain this seeming contradiction and to detect some striking resemblances between Cuba and the other Antilles.

First of all the so-called cretaceous deposits in the environs of Habana were explored. They can readily be examined in numerous exposures along roads and railway cuts in and near the capital. They are composed of white soft, sometimes nodular, fine-grained marls; of light-coloured, youngish looking, organogenetic limestones, which are seldom very pure, most often however contain some volcanic tuff-material; of true submarine tuffs; while sometimes also peculiar fine-grained limestone-breccias occur in the formation. In numerous spots I found in the limestones and in the submarine tuffs micro-organisms, which could be determined in microscopical sections. It now appeared that besides a number of Foraminifera, insignificant for the age of the formation, and besides Lithothamnium,

¹⁾ C. W. HAYES, T. W. VAUGHAN and A. C. SPENCER, *Geology of Cuba*, 1901 reprinted in 1918 by the Dirección de Montes y Minas at Habana.

²⁾ R. T. HILL, l.c.

³⁾ C. W. HAYES, T. W. VAUGHAN and A. C. SPENCER, l.c.

⁴⁾ L. TIPPENHAUER, *Peterm. Geogr. Mitteilungen*, 1899, p. 25—29, 153—155, 201—204; 1901, p. 121—127, 169—178, 193—199; 1909, p. 49—57. W. F. JONES, *Journal of Geology*, 26, 1918, p. 728—758.

⁵⁾ I. B. HARRISON and A. J. JUKES BROWN, *The geology of Barbados*, 1890, and other publications. G. WALL and J. SAWKINS, *Report on the geology of Trinidad*, *Memoirs Geol. Survey*, London, 1860.

also small Nummulinae and Orthophragminae occur in various localities and Nummulinae and Lepidocyclinae in other places. I encountered in various tuffish limestones between Ardaí and Arroyo Naranjo small Nummulites and Orthophragminae, while in limes, south-east of Regla, to the south of the bay of Habana and to the north of Guanabacoa, besides Nummulites also small Lepidocyclinae were found, which also occur in the railway-cut, north-east of Palatino (the finding-places are marked on the accompanying map).¹⁾ This "Older Habana-formation" is intensely folded, with dominant W—E. strike, and rapidly alternating steep dips, so that no positive opinion can be formed about the thickness of the whole complex of layers with its few well-continuous sections. This thickness however is sure to be very considerable. It is evident that this formation, which contains Nummulites and Orbitoides, and which, in concurrence with SALTERAIN (l. c.) was generally mistaken for cretaceous, is of a distinctly more modern type, being nothing else but the well-developed and intensely folded eocene, which we recognize with the same tectonic and partly also with the same petrographic features in so many localities of the Antilles. The occurrence of Orthophragmina implies that part of this intensely folded formation is decidedly eocene. We will endeavour to ascertain whether perhaps subsequent parts of the Tertiary are represented in this complex.

If the fossils, occurring in the "Older Habana-formation", had been found in Europe or Asia, there would be no doubt whatever about the occurrence also of oligocene and maybe even of old-miocene rocks in this complex, as in Europe as well as in Asia Lepidocyclinae are characteristic of the oligocene and the older miocene (Stampian to Burdigalian). However, in America Lepidocyclinae have been found also in unmistakably eocene deposits,²⁾ so that their occurrence in the vicinity of Habana is in itself no evidence at all. Now, the American species in positively eocene rocks (south-eastern part of the United States), are all large species, except one (*L. floridana* Cushman with a diameter of 4—8 mm.). In San Bartholomew (*L. antillea* Cushman with 5 mm.) and in the zone of the Panama-canal (*L. Macdonaldi* with 5—7 mm.) there occur, it is true, some smaller species in rocks, taken to be eocene, but the age of these deposits is not so well established as that of the

¹⁾ It is a pity that the names in the map are rather illegible but with the aid of a reading-glass it will be possible to recognize most of them.

²⁾ J. CUSHMANN, U. S. Geological Survey, Professional Paper, 125 D, 1920.

T. W. VAUGHAN, Proceedings First Pan Pacific Conference, Honolulu, 1921, p. 754—755.

formations of the South-east of the United States. Now, in the Habana rocks, described above, large *Lepidocyclus* are absolutely lacking; they contain only dwarf-species which — as experience in Asia and Europe has taught us — are more or less indicative of younger formations, so that part of the “Older Habanaformation” must very likely still be referred to the Oligocene. And this is not all. In the city of Habana and west of it the Older Habanaformation is overlain by rocks of quite similar petrographic habitus, but they are much less disturbed. These rocks of the „Younger Habanaformation” (organogenetic limestones, white and yellow marls, submarine tuffs) form namely a monocline, whose core still exhibits steep dips — up to 40° and higher —. The younger portions of this formation, however, which in its totality is dipping towards the sea, are much less steep. In the suburb of Vedado the marls of this formation are overlain by coral-limestones which are also dipping down towards the sea. The rocks of this “Younger Habanaformation”, which are so beautifully exposed in the marlpits of Puentes Grandes and of Cienaga and at the Castillo del Principe, are lying unconformably — as the accompanying map indicates — on the rocks of the “Older Habanaformation”: while the strike of the older rocks is E.—W., that of the younger is about N.E.—N.N.E. The facts, however, that in the deeper parts of the younger formation the layers are very sharply inclined, and that there is a remarkable petrographic similarity between the two formations tend to show that the stratigraphical gaping between the two formations is only very inconsiderable; nay, in all probability, the unconformity is only “tectonic”, is originated during the folding, and the two formations succeed each other most likely without a significant stratigraphical gap.

Now, M. SANCHEZ ROIG¹⁾ has for several years been collecting fossils from the marlpits of Cienaga. It is especially the teeth of *Selachii* that were encountered here. They point to a miocene age, while the more southern limestones of Vedado belong even to the Pliocene.

The foregoing no doubt justifies the conclusion that the rocks of the “Older Habana formation” belong partly to the eocene, partly to the oligocene, that the tertiary orogenetic movements in this part of Cuba began towards the close of the Oligocene, and that they continued even in the Pliocene.

So while in the North the layers of the “Older Habanaformation” are overlain unconformably by miopliocene rocks, which have still

¹⁾ M. SANCHEZ ROIG, Boletín de Minas, Habana, N^o. 6, 1920.

co-operated in the crustal movements, in the South near Arroyo Narranjo limestones are overlying the "Older Habanaformation", which are perfectly horizontal and can be traced southward as far as Guira, invariably in horizontal position. Near Arroyo Narranjo these limestones, which in their habitus differ greatly from the rocks of the "Older Habanaformation", are coastal limestones; farther to the south also Globigerina limestones occur. As a matter of fact these limestones, which have had no share in the latest orogenetic movements, must be of more recent date than the miocene rocks of the "Younger Habanaformation" and belong consequently to the Youngest Pliocene or Pleistocene. These limestones, which the Geological survey-map of North-America¹⁾ still marks as Old Tertiary, have lent support to the opinion that the Cuban Tertiary is only feebly folded, and that the Tertiary constitutes only a thin varnish overlying the older formations.

This does away with the seeming contrasts between Cuba and the other Antilles and replaces the island in the homogeneous range of the Antillean Cordillera.

In an excursion to San Diego de los Baños, about 100 k.m. to the west of the capital I encountered also here a well-developed and intensely folded eogene formation; to the North of this small town mesozoic limestones emerge, but farther to the south intensely folded rocks (strike E.-W.) are exposed everywhere — especially submarine tuffs — containing Lithothamnium, Nummulites and Orthophragminae. Globigerina marls also occur.

The Petrographic composition of the Cuban Tertiary is interesting also in other respects. First of all, in the Older as well as in the Younger Habanaformation limestones occur that, being examined microscopically, appear to contain much young volcanic material, nay in many cases, even change into true calcite-poor, submarine tuffs. Sharp angular splinters of plagioclase and quartz are numerous. Likewise numerous grains present themselves, of a substance containing plagioclase microlites, granules of ore and glass, which are to be considered as ground-mass fragments of an andesitic or dacitic rock. Similar eogene, submarine tuffs were also recognized in the Tertiary of San Diego. Much volcanic material also occurs in miocene deposits of a shallow sea (coralligene limestones, marls, calcareous sandstones and finely granular conglomerates), which are excellently exposed in the Yumurí cleft near Matanzas, about 75 k.m. east of Habana. On the contrary volcanic material seems to be lacking entirely in the very young, horizontally disposed limestones

¹⁾ B. WILLIS, l.c.

found near Arroyo Naranjo, Rincón, San Antonio de los Baños and Guira. In one of the younger portions of the Yumurí cleft-profile feldspars were so numerous that they could readily be examined in the pulverized rock. All the splinters that were examined, had a higher refractive index than canada balsam, so that there is a complete lack of orthoclase and albite. Among 20 splinters examined 13 had a higher, 7 an equal or a lower refractive index than eugenol (1.546), so the latter belong to oligoclase. Nearly all the splinters have a lower refractive index than nitrobenzol (1.556), so that among the larger feldspar splinters, which are of course fragments of phenocrysts from the dacitic-andesitic rocks, from which also the ground-mass originates, no plagioclases occur that are more basic than andesine¹). The effusive rocks supplying the material for submarine tuffs, must then have been a highly acid, potassium-poor dacite i.e., a rock in all points of the type of the "Pacific Rock".

It should be observed that the fragments of the ground-mass occurring in the tuffs, very often have a diameter of 1 mm. It is not out of the bounds of possibility of course, that similar volcanic material could have reached Cuba during an eruption of rather remote volcanoes, if at the time of the eruption a violent storm had been blowing in the direction of the island. The coarseness of the fragments, however, together with the very high frequency of volcanic material in formations extending from the eocene into the pliocene in localities nearly 200 k.m. apart, indicate that this material has not "come over" under "peculiar" circumstances from far-away volcanic centra. These submarine volcanic tuffs that are so widely diffused both stratigraphically and geographically, must be regarded as evidence that in the Tertiary the volcanic activity in the Antillean region extended over a much larger area than at present and that it did not settle down before the close of the Tertiary. This fact also tends to strengthen our view that the Antilles are geologically homogeneous.

It is likewise deserving of note, that no remains whatever are to be found of the volcanoes that must have existed as late as the latter half of the Tertiary in the neighbourhood of Cuba. This proves that already since the beginning of the Tertiary Cuba must have been subject to violent disturbances, where denudation destroyed rapidly what had been built up by volcanic and orogenetic processes.

¹) The refractive indices of the fluids used in the Utrecht geological institute for the determination of the refractive indices of minerals, have been verified only a short time ago by Prof. SCHOORL for which we tender our thanks.

Presently we shall see that other facts also corroborate this hypothesis.

In the vicinity of Habana a deeply weathered serpentine-massif (see sketchmap) has long (SALTERAIN l. c. and others) been known. In two localities — south of Guanabacoa and due south of the bay of Habana — quartzamphibole diorites are found as a dyke. These moderately acidic plagioclase rocks forcibly reminded me of the granular crystalline rocks of the "Pacific type", described by HÖGBOM (lc.) and derived from the Virgin Isles. The feldspars of this quartz-amphibolediorite all had a refractive index higher than canada balsam, but the refractive index of most of them was lower than that of quartz, to which they often are contiguous in the microscopical sections. Consequently they belong to the acid portions of the plagioclase series. Indeed the fact that this rock is poor in potassium and comparatively rich in silicic acid (much quartz and many acidic plagioclases) reminds us forcibly of many "Andes-rocks". Also by the occurrence of granular rocks of this type Cuba is united to the American continent on the one side and on the other to the Virgin Isles.

When perusing the literature concerning the Antilles we are impressed with an other incongruity between Cuba and the other Antilles. Already long ago young Radiolaria-bearing deposits became known in Barbados (HARRISON and JUKES BROWN, l. c.) which many geologists regard as true deepsea-deposits. R. T. HILL also described tertiary Radiolaria-deposits in the east of Cuba (Baracoa). However, whereas in Barbados the Radiolaria deposits overlie unconformably the older tertiary — which developed there as a terrigenous deposit — and have only been subject there to faulting and not to folding, the Radiolaria deposits of Baracoa have a steep dip, so that there seemed to exist a stratigraphical incongruity between these deposits in the two islands. In the neighbourhood of Habana I encountered Radiolaria-bearing rocks in two levels of the Tertiary. In the first place white marls in the "Older Habanaformation" near Cerro, with a dip of 75° southward. They are entirely filled up with Radiolaria that belong for the major part to the Spumellaria, for a small part however also to the Nassellaria (fig. 1). Secondly, in the most recent part of the "Younger Habanaformation", i. e. in the marlpits of La Cienaga, white Globigerina marls occur which contain a not inconsiderable amount of Radiolaria. Now it is very well possible that the Radiolaria-marls of Cerro are the equivalent of those of Baracoa in East-Cuba, whereas the Radiolaria-bearing Globigerina marls of La Cienaga are stratigraphically more like the deposits in Barbados. Also the contrast which apparently exists in

this respect between Cuba and some of the other Antilles finds an explanation in the above.

Indications of the homogeneity of the row of Antilles can also be found in the older formations of Cuba. As stated previously, of late years Malm-ammonites have been found near Viñales, in the most western part of Cuba. These Upper-jurassic layers, which dip away to the North at a rather small gradient, are overlain by thick, old-looking grey limestones with intermediate layers of sandstones, which, therefore, are probably to be referred to the Cretaceous system. In one place I found in these limestones small nests of red chert; under the microscope this red chert appeared to be a true Radiolarite, very much like the Radiolarites so widely diffused in the mesozoic rocks of the southern Moluccan-cordillere (fig. 2). The geological institute at Utrecht possesses a number of rocks from the islands of Curaçao, Bonaire and Aruba, collected by Dr. I. BOLDINGH. Among the rocks from Bonaire and Curaçao it was not difficult to recognize Radiolarites — probably mesozoic — bearing close resemblance to those from Cuba.¹⁾ This is not all. In the coral-limestones of the Yumuri-cleft near Matanzas coarse clastic material was found; boulders to a maximum of 7 mm. in diameter. Four of them were ground, of which two appeared to be red radiolarites like those found to the north of Viñales, while in our days mesozoic sediments are lacking in this part of the island.

It is evident, therefore, that such a peculiar sediment as the mesozoic, red radiolarite is found at the extremities of the Antillean region: in the most western part of Cuba and in Bonaire and Curaçao. This, no doubt, warrants the assumption that the Antillean region is one continuous whole, parts of which, in spite of their different appearance, have many features in common, that point to an historical homogeneity.

From the occurrence of much volcanic material in the whole tertiary of Cuba, in the neighbourhood of which no volcanoes exist any more, we may conclude that the island must have been subject to great geological disturbances in recent times. A similar conclusion may be deduced from the great abundance of boulders of cretaceous Radiolarites in the miopliocene of the Yumuri-cleft, as these boulders

¹⁾ K. MARTIN, Bericht über eine Reise nach Niederl. West Indien, II, 1888, p. 28 and 73 and J. H. KLOOS, Samml. Geol. Reichs-Museums, Leiden II, 1, 1887, already demonstrated the occurrence of Radiolaria-bearing rocks in Curaçao and Bonaire. From their descriptions it is not evident, however, that we have to do here with typical Radiolarites, which at that time did not receive so much attention from geologists as nowadays.

point to a powerful post-eocretaceous mountain-building by which the deep-seated Radiolaria-deposits were uplifted beyond the sea-level, while in the Tertiary the mountains were entirely denuded again.

In the foregoing Radiolaria-bearing deposits have been described from three levels of the series of sediments of Cuba: a fourth level can still be added. Between Bacuranao and the boring-field which is located to the north of this village, green sediments were observed in the centre of the serpentine-area. These sediments are distinctly seen to dip away below the serpentine. Under the microscope they appeared to be in part volcanic tuffs, in part remarkable radiolarites, which consist chiefly of skeletons of Radiolaria, but also contain spiculae of sponges, while the silicic acid of the Radiolaria as well as of the sponges spiculae is still perfectly amorphous (fig. 3). These siliceous sediments are closely connected with the volcanic tuffs; not only do the Radiolaria-layers and the tuffs possess equal dip and equal strike, but sometimes the siliceous sediments contain splinters of plagioclase, and in one of the microscopical sections the tuff even passes into the siliceous sediment. These Radiolarites of Bacuranao certainly belong to an older level than the tertiary Radiolarites, as the former dip away below the serpentine, whereas the whole tertiary is more recent than the serpentine, whose water-worn fragments are found here and there in the tertiary limestones and calcareous sandstones. They belong moreover to another level than the red Radiolarites of Viñales and Matanzas, for the thick limestones bearing the red Radiolarites of Viñales are not found near Bacuranao. The siliceous sediments are closely related to the Cuban serpentines.

Now it is very remarkable that in Cuba such extreme deposits as Radiolarites appear in four different levels. Even when not assuming that Radiolarites are true deepsea deposits, we must be convinced that the formation of these calcium-free or calcium-poor siliceous sediments requires conditions that do not exist in the shallow epi-continental seas. At all events the occurrence of these deposits in at least four levels of the island of Cuba justifies the conclusion, that the area in which the island is now situated, was in the latter half of the Mesozoicum an extremely restless region, where now deposits of a shallow epicontinental sea (sandstones in the Chalk, Nummulites and Orbitoide-bearing limestones in the Tertiary), then again such peculiar sediments as Radiolarites¹⁾ could be formed.

¹⁾ One more fact may be adduced to confirm the conception that at least one level of the Radiolaria-bearing deposits in Cuba is formed, if not in a true deep-

There are, indeed, two more arguments for the conclusion that Cuba has ever been a very inconstant region, at least since the Tertiary.

In the outset we reminded the reader that already SUESS, WICHMANN and MARTIN had pointed out the analogy between the Antilles and the southern Moluccas, which analogy is brought out in a similar arrangement of the tectonic elements. Two points have been discussed above to emphasize this analogy. In the first place the occurrence of Red Radiolarites, so very typical of the Mesozoicum of the Moluccas, in the two extremities of the Antilles. In the second place the conception that in the latter geological periods the Antillean region was so extremely restless. It is known, indeed also of the southern Moluccas, that their region was very changeable, and was characterized by great instability in the relations of land and sea: also there the formation and the denudation of mountains took place in such rapid succession, that it is difficult to disentangle the development of the geological history. We may add even one more detail in comparing the instability of the Antillean region with that of the southern Moluccas. In the Antilles it struck us that in one and the same island Radiolaria-deposits occur at least in four different levels. Why, also of the island of Rotti, near Timor, BROUWER has described ¹⁾ Radiolaria-bearing deposits in three totally different levels: Upper Trias, Malin and Tertiary.

Utrecht, May 1922.

sea, anyhow in a sea of considerable depth. In the white marls of La Cienaga, where many Globigerina and also numerous Radiolaria occur Sanchez-Roig (l.c.) has found numerous teeth of Selachii. A large number of these teeth (though by far not all) display the peculiarity that only the enamel of the teeth is left, while the dentin has completely disappeared. This state of preservation is exclusively characteristic of Selachii-teeth that are encountered in the deepest sea and in deepsea deposits.

Cf. MOLENGRAAFF and BEAUFORT, Proceedings XXIX, 1921, p. 677—692.

¹⁾ H. A. BROUWER, De Nederlandsche Timor Expeditie, III, 1921. Geologische onderzoeken op het eiland Rotti.

DESCRIPTION OF THE PLATES.

Fig. 1. White Radiolariamarl. Older Habanaformation. $\times 26$.

Fig. 2. Red Radiolarite. Viñales. $\times 26$.

Fig. 3. Silicious rock with Radiolaria and Sponge-spiculae. Bacuranao. $\times 26$.

Fig. 4. Geological Sketchmap and transverse profile of the vicinity of Habana.

— . — . — Railways.

ABC—CD Line of Profile.

S. Serpentine.

D. Quartzhornblendediorite.

A. Petroleum Rigs.

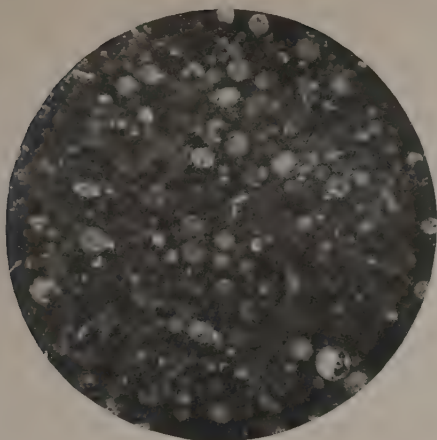


Fig. 1. $\times 26$.

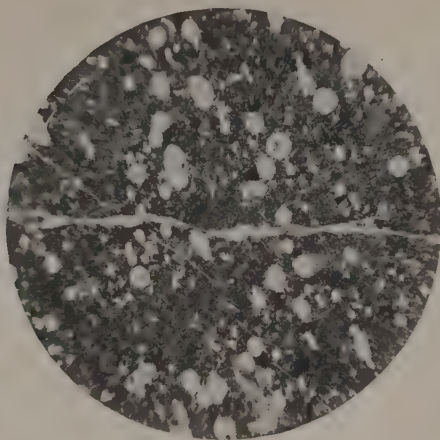


Fig. 2. $\times 26$.

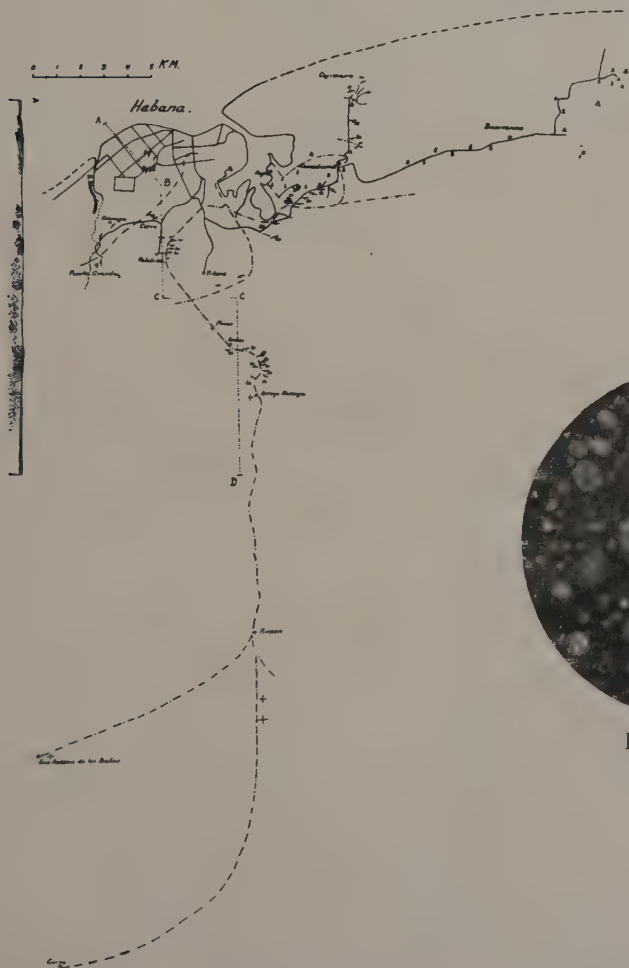


Fig. 4.

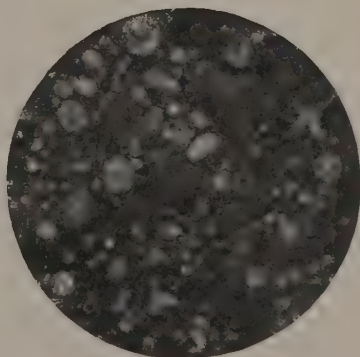


Fig. 3. $\times 26$.

Bio-chemistry. — "*Changes in Milk due to Sterile Inflammation of the Udder.*" By Prof. B. SJOJLEMA and J. E. VAN DER ZANDE.
(Communicated by Prof. C. EYKMAN.)

(Communicated at the meeting of May 27, 1922).

The examination of a number of samples of abnormal milk from cows suffering from clinically observable affections of the udder, as well as from cows in which clinically no anomalies of the udder were noticeable, impressed us in 1921 with the idea that too great an importance is ascribed to streptococci as causative agents of the secretion of abnormal milk. We found for instance that in very abnormal milk streptococci are often absent.¹⁾ We, therefore, decided to go further into this subject and produced sterile inflammation of one of the quarters (R. F.) of the udder of a milch-cow in full lactation, with the aid of a suitable injection. On the suggestion of Prof. PAIMANS a solution was administered of silver-nitrate of 0,2 %.²⁾

In the same cow a sterile abscess had previously been developed through injection of oil of turpentine in the region of the neck with a view to ascertain whether such a sterile inflammation exerted any influence on the secretion of milk. We were induced to do so, because in a previous investigation in our laboratory anomalies had been found in the milk yielded by animals which were affected by inflammation of quite other parts of the body than the udder.

The results obtained after the injection of oil of turpentine need not take us long. Although a considerable abscess had developed, the composition of the milk did not undergo a notable change, neither during the development, nor after the abscess had become mature.

Once the sediment of the milk from one of the quarters had increased a little, of which the abscess may not have been the

¹⁾ Our report pertinent to the matter in question appeared in *Tijdschrift voor Vergelijkende Geneeskunde* enz. Band 7 1922.

²⁾ We were in a position to prosecute this inquiry thanks to the aid of Prof. W. J. PAIMANS and the Conservator for Obstetrics, Mr. J. A. J. M. KIRCH, whose assistance we acknowledge with gratitude.

cause. It would seem, therefore, that a sterile inflammation does not affect the secretion of milk in the same way as a bacterial inflammation has in our earlier researches repeatedly proved to do; this result could be expected.

The effect of the sterile inflammation of the udder with silver-nitrate solution was quite different. The very next day (9 March) the composition of the milk had changed very much, as was also the case on the following days, when the milk presented also a very abnormal aspect.

Gradually composition and aspect improved; however, this quarter became choked before the milk was quite normal; at all events not a trace of milk could be drawn on March 19 and following days. The examination of the milk-samples gave the results tabulated on the following page. For the sake of comparison we have also tabulated the figures of some abnormal milk-samples *with* (N°. 164 and 142) and *without* (N°. 181 and 267) streptococci, which samples were examined in 1921. For the same reason we included the figures obtained from the same quarter (R. F.) of the injected cow before this treatment (N°. 343 and 337) and from other quarters (N°. 385 and 381) after the injection.

The table shows that the milk from the quarter injected with silver-nitrate possessed, — with the exception of the presence of streptococci, — all the properties of milk from animals, suffering in a high degree from udder-affections e.g. streptococci mastitis). Acidity, p_H , sediment after centrifugation in Trommsdorff-tubes, leucocytes, chlorin-, and lactose-content, were all changed in the same measure,¹⁾ as were also the total protein-content and the calcium-content.

Furthermore the content of total, combined-, and free carbonic acid appeared to have increased, just as in milk from cows with diseased udder. This anomaly and its connection with the hydrogen-ions concentration of milk has been pointed out in 1919 by L. L. VAN SLIJKE and J. C. BAKER²⁾.

Lastly, the tryptophane-content appeared to be considerably increased. In 1921 we found this content in abnormal milk (derived from diseased udders), and in colostrum to be very high. This is no doubt due to the occurrence in these kinds of milk of much protein, which is identic with, or related to the globulins of bloodserum, just as the other anomalies of the milk from cows with diseased

¹⁾ Milk containing streptococci has sometimes a high degree of acidity.

²⁾ Journ. Biol. Chem. 40. 335 (1919).

No. (quarter).	Ordinary Acidity	Oxalate Acidity	p.H.	Sediment Tromms- dorff (resp. number of leucocytes)	Chlorin mgrs. per 100 c.c.	Lactose %	Katalase figure	CaO mgrs. per 100 c.c.	Tryptophane (after precipitating with alum) mgrs. per 100 c.c.
381 (R.F.)	2.5	—	—	0.35 % ¹⁾	—	—	—	120.2	110 ⁶⁾
382 »	3.3	—	—	2.2 » ²⁾	298.4	—	—	—	—
385 »	5.3	1.3	6.98—7.06	(mucus) ²⁾	280	— ⁵⁾	—	—	300
387 »	4.8	0	6.75—6.82	0.5 % ³⁾	153.6	—	—	196	90
164	4.8	1.2	6.8—6.9	±1.5 c.c.	290	1.3	6.9	101	— streptococci occur
142	5.6	0.8	6.75—6.82	0.5 % ³⁾	149.	—	3.5	188	— " "
181	4.4	0.4	6.9—6.98	0.7 »	220	3.2	—	179	— " absent
267	4.6	0.1	6.75—6.82	450 000	169	—	7	—	— " "
343 (R.F.)	7	2.3	—	0.35 % ³⁾	89.5	4.8	—	242.5	— of "silvernitrate" cow before
337 »	7.4	—	—	0.2 »	107.7	—	—	—	norm. treatment.
385 L.F. and L.B.)	8.6	4.2	6.5—6.6	—	—	—	—	—	from other quarters of the
381 (L.F.)	7	—	—	0.1 % ⁴⁾	84.3	—	—	—	"silvernitrate" cow; drawn

¹⁾ rather many leucocytes.

²⁾ full of leucocytes.

³⁾ few leucocytes, many cells with rounded nucleus.

⁴⁾ number of leucocytes normal.

⁵⁾ Milk drawn one day later contained 2.7 % lactose.

⁶⁾ Milk drawn one day later contained 348 mgrs. of tryptophan.

udders are connected with the transit of bloodplasma-components in abnormal milk. While 100 c.c. normal milk — after removal of casein and fat with the aid of potassium-alum contain according to our investigations about 14—20 mgrs. of tryptophane, as much as 348 mgrs. occurred in the milk-samples after the injection of silvernitrate, that is about twenty times more.

The determination of the tryptophane-content, easily executed by the colorimetical method of VON FÜRTH and NOBEL¹⁾, is no doubt one of the most accurate methods for examining the normality of milk.

The foregoing experiments tend to show that the anomalies characteristic of streptococci-containing milk, arise also from sterile inflammation of the udder-tissue, so that streptococci need not always be essential to the occurrence of similar anomalies. The question whether, in the case of streptococci-mastitis, these bacteria are very often only of secondary importance can of course not be answered on the basis of this investigation.

*From the Chemical Laboratory of the Veterinary
University of Utrecht.*

¹⁾ Biochem. Zts. 109. 103. (1920).

Microbiology. — “On *Bacillus polymyxa*”¹⁾. By Prof. M. W. BEIJERINCK and L. E. DEN DOOREN DE JONG.

(Communicated at the meeting of September 30, 1922).

If the species-conception is taken in a not too limited sense, the closely related, but not identic forms mentioned in Note 1, may be said to comprise the only known aërobic spore-forming bacterium-species, which causes fermentation in a sugar-containing medium. We call it *Bacillus polymyxa*.

It is rather generally spread in fertile soils; its properties are very characteristic and give rise to interesting experiments. The production of acetone first observed by SCHARDINGER, has in the later years drawn attention on this microbe, but the quantity formed is small and from malt or potatoes it does not amount to 1 % of the weight. But the conditions for its formation are not yet well-known and might perhaps be greatly improved as to the quantity. Alcohol is also generated and to a somewhat greater amount than acetone. Besides, a little acetic- and formic acid seem to be produced. Particularly the secretion of the enzyme pectinase and of much slime by the chief variety is of interest.

¹⁾ The literature of this Bacterium and its nearest relations is to be found under: *Clostridium polymyxa* PRAZMOWSKI, *Granulobacter polymyxa* BEIJERINCK, *Bacillus macerans* SCHARDINGER and *Bacillus asterosporus* A. MEYER. — A. PRAZMOWSKI, Entwicklung und Fermentwirkung einiger Bacteriën. Dissert. Leipzig 1880, p. 37. — TH. GRUBER, Identifizierung von *Clostridium Polymyxa* PRAZMOWSKI, Centralbl. f. Bakteriöl. 2te Abt. Bd. 14, 1905, pag. 353. — F. SCHARDINGER, *Bacillus macerans*, Acetonbildender Rottebacillus, Centralbl. f. Bakt. 2te Abt. Bd. 14, 1905, pag. 772. Zur Biochemie von *B. macerans*. Centralbl. f. Bakt. 2te Abt. Bd. 19, 1907, p. 161. Kristallisierte Polysaccharide aus Stärke durch Mikroben. Centralbl. f. Bakter. 2te Abt. Bd. 22, 1909, p. 98 and Bd. 29, 1911, p. 189. — A. MEIJER und G. BREDEMANN, Variation und Stickstoffbindung durch *Bacillus asterosporus*. Centralbl. f. Bakteriöl. 2te Abt. Bd. 22, 1909, p. 44.

The name *asterosporus* is derived from 9 or 10 rims on the exosporium of the oblong spores, which make the transversal section star-like. By abundant feeding, as on wort-gelatin, many rodlets change into narrow clostridia containing somewhat granulose, colored blue by jodine; so the species may also be called *Granulobacter polymyxa*.

Accumulation and occurrence.

Long ago the following experiment for the accumulation of this species was described ¹⁾.

Coarsely ground rye with some chalk and inoculated with fertile garden soil is mixed with water in a deep beaker to a thick solid paste, boiled during some seconds to kill the non-spore-formers and cultivated at 25° to 30° C. As the spores of *B. polymyxa* soon die at boiling, the heating must last but a short time. After a few days the surface is covered with a coherent film of *B. mesentericus* ²⁾ and other closely related species, while in the depth a butyric-acid fermentation takes place, usually simultaneously with butylic-alcohol- and polymyxa fermentation.

It is clear that this accumulation reposes essentially on a temporary anaërobiosis of *B. polymyxa*, which can also grow aërobic and so behaves like the alcohol yeast and the *Aërobacter-Coligroup* among the bacteria. The rye produces the sugar causing the fermentation, i.e. the source of energy, which makes the anaërobiosis possible so long as the "excitation oxygen" is still sufficiently present, albeit chemically non-demonstrable, whereas the want of "oxidation oxygen", which is required for aërobiosis in much larger quantity as source of energy, is temporarily excluded. PASTEUR's statement: "la fermentation est la vie sans air" is evidently applicable to *B. polymyxa*.

By sowing out the fermenting matter from the depth on wort-agar, ordinarily already after few days the polymyxa colonies become visible as lumps of slime, together with the unavoidable flat spreading colonies of *B. mesentericus*.

This method can only produce those varieties of *B. polymyxa* which are able to resist a relatively high concentration of the food. Another accumulation method by which also forms adapted to a lower concentration of food are obtained is based on the aërobiosis of our bacterium.

After the observation had been made that flasks of boiled wort, not sufficiently sterilised, were not seldom spoiled at the low temperature of 15° C. by the development of *B. megatherium* and never by *B. mesentericus*, whose germs were certainly also present, the question

¹⁾ M. W. BEIJERINCK. De butylalcoholgisting en het butylferment. Academy of Sciences. Amsterdam 1893.

²⁾ This film may be colourless, brown, red, and even jet black according to the accidentally present varieties of *B. mesentericus*. The black form is rare and sometimes obtained by the "mesentericus experiment" with unwashed currants (boiling with chalk, cultivating at aëration at 30° to 40° C.).

arose: which are the aërobic spore-forming bacteria, which can develop at temperatures of 15° C. or lower and under favorable feeding conditions? We knew already that the obtaining of *B. megatherium* might give an answer to the question, for example in case the spores of this species were only present with those of *B. mesentericus*, but it seemed possible that free competition with the soil bacteria would exclude *B. megatherium* and that some other species could appear. The chief aim of the experiment was to exclude *B. mesentericus*, the common hay bacterium, which produces substances very noxious to other species, and this is to be reached by the low temperature, as the minimum for the growth of this species is at about 20° C. The simultaneous development of *B. megatherium* is of less importance as it is innocuous to other kinds. Of course we had to reckon with the butyric-acid and butylic fermentations, which may very well occur at 15° C, but strong aëration prevents them efficiently.

Although we could expect that the one or more species that were to develop under the chosen conditions would possess a higher temperature optimum than that used by us, we had not to fear a failure if only we cultivated above their minimum.

Knowing that the spores of some spore-formers, for example those of the butylic ferments, and thus perhaps, too, those of the species we sought for, could not or hardly resist boiling, the heating of the culture liquid containing the inoculation material and wanted for killing the non-spore forming species, was not continued much above 85° or 90° C. and only for a few seconds. We used flasks half filled with about 30 cM³ liquid, and in order not to miss somewhat rarer species, we inoculated with so much soil that on the bottom a layer of about 1 cM precipitated. This soil had previously been well-divided and freed from coarse particles. In such a thick layer a beginning of anaërobiosis is possible, but by shaking, butyric-acid or butylic fermentation may easily be stopped.

For food we used at first malt-wort, diluted to 2° to 5° BALLING, later broth-bouillon with 2% to 5% cane sugar, or glucose. Addition of chalk is not absolutely wanted for the success of the experiment but its presence proved favorable.

After we had ascertained with pure cultures of *B. polymyxa* that ammonium salts, nitrates and asparagine are very good sources of nitrogen, we also accumulated with sugars and ammonium sulphate, in a solution of tapwater 100, 2 to 5% glucose or cane sugar, 0.05% $(\text{NH}_4)_2\text{SO}_4$, and 0.02% K, HPO_4 with some chalk. The execution of the experiment is as above, but after pasteurising,

the butyric-acid fermentation must be more completely excluded than when using broth-bouillon or malt-wort. For although the latter liquids contain an excellent nitrogen food for *B. polymyxa*, they are of less value for the butyric-acid ferments, for which the ammonium salts are preferable. Hence, in this case it is advisable to use a large Erlenmeyerflask, as the great volume of soil which sinks to the bottom as inoculation material, can then be better aerated, by which butyric fermentation is prevented.

Although the growth is slow at the low temperature the liquid becomes distinctly turbid and in most cases this is accompanied with fermentation. This fermentation especially awakened our attention as we had expected an accumulation of *B. megatherium*, which causes no fermentation at all.

As the *Coli*- and *Aërogenes* fermentations had been prevented by the previous heating, the butyric-acid and butylic fermentations by the aëration, we now expected that the fermentation of *B. polymyxa* was obtained, and this was confirmed by the pure culture. The fermentation which is chiefly an alcoholic one, proves that our bacterium belongs to the facultative (temporary) anaërobes, and the examination of the gas showed that it is almost pure carbonic acid.

One of the most notable qualities of *B. polymyxa* is its secretion of pectinase, i. e. the enzyme by which some microbes dissolve the central lamellum of plant tissues, thereby disintegrating them into cells. Hence, *B. polymyxa* like *B. mesentericus* may under certain circumstances play a part in the retting of flax, although the real agent in this case is the anaërobic *B. pectinovorum*.

Beans, peas and other plant seeds, left to spontaneous corruption, may change into rich cultures of *B. polymyxa*, the cell-walls of cotyledons and of endosperm being easily attacked by pectinase, whereby the interior of the seeds is changed to a pulpy mass¹). For the preparation of a pure culture this method is less recommendable than the two foregoing accumulations, on account of the numerous hay bacteria which thereby simultaneously develop; it is, however, a good way to get an initial material for the said accumulations themselves.

It seems to us that the generality of *B. polymyxa* in our surroundings and particularly in the soil should be explained by its pectinase secretion, which must give this species, in combination with its little want of air, a great advantage over the other saprophytes.

¹) The enzyme seminase, which changes the endosperm of the Leguminosae (*Indigofera*, *Ceratonia*) into mannose, is perhaps identic with the pectinase of *B. polymyxa*.

The very common presence of *B. polymyxa* in the bark of the nodules of the Leguminosae is certainly also a direct consequence of its pectinase production. Its presence there is of so general occurrence, that it reminds more of symbiosis than of saprophytism. In the bacteroid tissue *B. polymyxa* is however completely absent.

Properties of the colonies.

The colonies on agar as well as those on gelatin are characteristic. On malt-wort gelatin they resemble at first thin, watery, sideways quickly extending, slowly liquefying layers, which by and by become deeper and cloudy by their strong growth. At length the gelatin is completely liquefied and then these cultures resemble those of common hay bacteria. On malt-wort agar there is a profuse production of slime, whence very distinct voluminous and wrinkled colonies appear. The slime attracts part of the pigment from the wort-agar thereby becoming brown-coloured, which gives a characteristic appearance to the colonies.

On glucose-kalium-phosphate-ammonium-phosphate-agar they become glass-like transparent, somewhat resembling glass globules, so peculiar that at estimating the number of germs in soil samples, they may directly be recognised and counted. Silica plates, saturated with food, also produce such drop-like colonies from soil. Some varieties form much less slime than others and this slime is either tough or soft.

Microscopically those with soft slime consist of much shorter rodlets. Hence, one is at first disposed to think of different species, but further research shows the similarity, which is the more convincing, when beside the natural varieties, the mutation phenomena in the pure cultures are studied. On cane-sugar-asparagine agar many colonies, at first quite homogeneous and soft, when getting older produce small, rather solid, transparent, secondary colonies which, after separation from their surrounding (which is not easy) prove to be constant. On malt-wort agar the variety with tough slime, when growing older produces extensive, flat secondary colonies, showing a hereditary loss of the factors for slime formation.

In liquid nutritive media the form resistant to high concentrations of the food gives remarkable cultures.

In a malt-wort of 10° BALLING at 30° they consist of excessively voluminous slime masses, forming after one or two weeks a thick, coherent, floating film, inflated by carbonic acid, whilst no hydrogen is detectable. Only in the anaërobic butylic fermentation something of the like may be observed but then much hydrogen is present.

Even the most slimy *Aërobacter* forms produce quite different submerged cultures equally dispersed through the solution.

The vigorously fermenting slime varieties of *B. polymyxa* produce acetone, probably after the formula



To the products of the anaërobic fermentation belong in particular aethyl alcohol, with traces of acetic acid and formic acid beside some other products, such as butylic glycol, in small quantities.

The less slimy varieties of *B. polymyxa* can only live in food of lower concentration and spread through the solution as *Bact. aërogenes*. Also in other respects there is similarity between *Bact. aërogenes* and *B. polymyxa*, so that there is cause to conclude to a real relationship. Still there is a great difference in so far as *aërogenes* can assimilate many organic salts, a power quite absent in *B. polymyxa*.

Nutrition.

For the investigation of the substances which can be assimilated by *B. polymyxa*, the auxanographic method is very convenient, particularly in relation to the carbohydrates, *B. polymyxa* being a real "sugar bacterium", which produces much cell-wall matter, which makes the auxanograms very distinct. In judging the latter it should be kept in view that, beside pectinase, *B. polymyxa* produces diastase, invertase and emulsine. In presence of sugar various nitrogen compounds are assimilable, of which, however, only nitrogen is taken up. We preferentially used peptone, asparagine ureum, ammonium sulphate and saltpeter. Urease is not secreted; saltpeter is reduced to nitrite, not to nitrogen.

As in absence of sugar the carbon cannot be withdrawn from nitrogen compounds, such as peptone and asparagine, the growth, even on broth-bouillon-agar is but slight and is a criterion for the quantity of sugar present. Hence, if on this medium *B. polymyxa* is densely sown, only small, hardly visible colonies grow, consisting, however, of bacteria with abundant protoplasm and commonly motile. If on such a culture an assimilable carbohydrate is locally distributed, vigorous growth ensues, chiefly reposing on slime formation and a distinct auxanogram results, demarcated by the limit of diffusion of the substance. It is in fact the presence of a small amount of complete food at the starting of the experiment, together with excess of by themselves unassimilable nitrogen compounds, which enables the germs to change into small colonies, which

renders the further growth after addition of the carbohydrate very clear.

Most sugars and polyalcohols are readily assimilated by *B. polymyxa*. This we have ascertained for arabinose, glucose, levulose, mannose, galactose, cane-sugar, maltose, lactose, melibiose, raffinose, rhamnose, glycerin and mannite. On the other hand sorbite, dulcitol, erythritol and quercitol are not attacked. It is very notable that we did not find any organic salt assimilable by this organism.

The "sugar bacteria", to which *B. polymyxa* belongs, produce from carbohydrates much more visible cell-wall substance than protoplasm, if the carbohydrates exceed the nitrogen food and vice versa.

Hence, *B. polymyxa* may be found, as was observed above, in two microscopically greatly different conditions. At insufficient feeding with carbohydrates, for example on broth agar, it grows as highly motile rodlets, without slime wall; at copious feeding with carbohydrates, as immotile rodlets with a thick slime wall¹). This circumstance leads to the following experiment, only adapted to the variety of *B. polymyxa* which produces voluminous slime and grows strongly on malt-wort.

The bacterium densely sown on cane-sugar-kaliumphosphate-agar, containing but few nitrogen compounds, may form fairly large colonies consisting, however, almost entirely of the strongly swollen walls of the cells. By addition to the said medium of a few drops of complete food, for example a little broth or malt-wort, containing an excess of sugar, the slime walls grow surprisingly so that the plate covers with a relatively thick slime coat. This slime is built up of the sugars by one or more synthetically acting enzymes, that might be named "cytases" and should be considered as the genes or factors of the cell-walls.

This slime has the remarkable property of being able to become itself a source of carbon food, but only at the moment when all the cane sugar and all the assimilable nitrogen compounds have been used. If at this time some such nitrogen compound as ammonium-sulphate or asparagin are brought on the slime coat of the plate, the bacteria begin anew to grow and produce new protoplasm from their own cell-walls. This leads to the peculiar consequence, that an auxanogram is produced sinking deep into the layer of slime. For, by the growth the bulk of the bacteria is diminished, because the walls, which chiefly consisted of water and were very voluminous, disappear and are replaced by living protoplasm. So the appearance of the auxa-

¹) Medici give to the cell-wall of bacteria the singular name of "capsule".

nograms is quite changed when compared with the original state, for by their intense increase the opaque bacteria produce an also opaque auxanogram, whilst the original slime was transparent like glass. This proves that, in this case at least, the biological function of the slime is that of a reserve food.

In this experiment cane sugar was the food for the slime production; as hereby inversion takes place, glucose and levulose are probably the building materials of the slime; that these sugars are assimilated was stated above, and that glucose may also serve for the described experiment we ascertained particularly.

The other sugars have not yet been extensively examined from this point of view, but it seems that all give the same result. This leads to the conclusion that probably no more than two or three factors or genes (endoenzymes) are active in the production of the cell-wall. The problem is evidently of theoretic interest and deserves nearer research.

The wall-substance, which certainly belongs to the cellulose group and therefore may be called cellulane, must have a high power of attraction for water, for else its surprising volume cannot be explained. Nevertheless its molecules cannot be very small as they cannot diffuse at all in water. It is not colored by iodine, nor is it attacked by diastase. But as *B. polymyxa* may use it as a food-substance, this species evidently can excrete an enzyme which dissolves it. It is not improbable that this enzyme is pectinase, but this question is not yet answered. Should this really prove to be true, then the other question arises whether the so-called pectose of the central lamellum of the tissues of the higher plants may not also be a cellulose modification, as it is also easily dissolved by pectinase. This view seems to be much more acceptable than the current hypothesis: the central lamellum should be the calcium salt of an acid, isomeric with arabin-acid.

On the great similarity between pectinase and the seminase of the seeds of the Leguminosae, I already earlier directed the attention. That the latter enzyme does not attack true cellulose is in accordance with the same property of pectinase.

SUMMARY.

With a not too limited species-conception *Clostridium polymyxa*, *Granulobacter polymyxa*, *Bacillus macerans*, and *Bacillus asterosporus* may be brought to one single species: *Bacillus polymyxa*.

It is the only hitherto known aërobic spore-former, which, in

neutral sugar-containing media excites fermentation and thereby proves able to live as a temporary anaërobe.

The chief products of the fermentation are carbonic acid and alcohol. At the aërobic life a little acetone results, evidently from oxidation of sugar.

Anaërobic accumulation is possible in rye paste at 30° C. after short boiling. Aërobic accumulation takes place in dilute malt-wort or broth with 2 % to 5 % sugar, after heating at 85° to 90° C. or short boiling with much garden soil and cultivation at 15° C. by which *B. mesentericus* is excluded, whose growth minimum is at about 20° C.

The general distribution of *B. polymyxa* in decayed plants and its occurrence in the bark of plant roots and of the nodules of the Leguminosae reposes on the production of pectinase, which dissolves the central lamellum of the cellular tissues.

B. polymyxa forms much slime from sugar, which must be considered as cell-wall substance. Without carbohydrates or polyalcohols its growth seems impossible, hence it develops but slightly on broth agar.

The slime may serve as reserve food.

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Mathematics. — “On the Light Path in the General Theory of Relativity.” By Prof. W. VAN DER WOUDE. (Communicated by Prof. H. A. LORENTZ.)

(Communicated at the meeting of September 30, 1922).

In EINSTEIN'S theory the path of a ray of light is found by putting the condition that it is a geodesic null line in the four-dimensional time space¹). If accordingly we represent the line element of this time space by

$$ds^2 = \sum_{i,k} g_{ik} dx_i dx_k \quad . \quad . \quad . \quad . \quad . \quad (1)$$

the light path satisfies equally the equations of the geodesic as those of the null line

$$ds = 0 \quad . \quad . \quad . \quad . \quad . \quad (2)$$

As far as we know the remarkable relation existing between these differential equations, has not yet been pointed out. We shall prove that this may be expressed in the following way:

a geodesic having one element, i.e. one point with the tangent at that point, in common with a null line, is itself a null line.

In order to prove this we shall first give the equations of the geodesic a form different from the usual one (§ 1), as on account of (2) it is not desirable to take s for the independent variable. With a view to an application which we shall give later on, we take one of the coordinates of the time space for the independent variable.

We shall conclude by pointing out the (evident) physical meaning of the theorem.

§ 1. If the line element is represented by

$$ds^2 = \sum_{i,k} g_{ik} dx_i dx_k,$$

the equations of the geodesic are

$$\frac{d^2 x_\nu}{ds^2} + \sum_{\lambda, \mu} \left\{ \begin{matrix} \lambda \mu \\ \nu \end{matrix} \right\} \frac{dx_\lambda}{ds} \frac{dx_\mu}{ds} = 0 \quad . \quad . \quad . \quad . \quad . \quad (3)$$

¹) From this there follows for the statical field (g_{ik} independent of the time-coordinate x_0 and $g_{0l} = 0$ for $l \neq 0$) the principle of FERMAT for the minimum time of light in three dimensional space.

CHRISTOFFEL'S symbol $\left\{ \begin{smallmatrix} \lambda & \mu \\ \nu \end{smallmatrix} \right\}$ has here the meaning:

$$\left\{ \begin{smallmatrix} \lambda & \mu \\ \nu \end{smallmatrix} \right\} = \sum_{\tau} g^{\nu\tau} \left[\begin{smallmatrix} \lambda & \mu \\ \tau \end{smallmatrix} \right],$$

where $g^{\nu\tau}$ is the algebraical minor of $g_{\nu\tau}$ in the g -determinant divided by this determinant, and

$$\left[\begin{smallmatrix} \lambda & \mu \\ \nu \end{smallmatrix} \right] = \frac{1}{2} \left(\frac{\partial g_{\lambda\nu}}{\partial x_{\mu}} + \frac{\partial g_{\mu\nu}}{\partial x_{\lambda}} - \frac{\partial g_{\lambda\mu}}{\partial x_{\nu}} \right)$$

As independent variable we chose one of the coordinates, e.g. x_0 . In this case

$$\frac{dx_{\nu}}{ds} \times \frac{ds}{dx_{\nu}} = \frac{dx_{\nu}}{dx_0}; \quad \frac{d^2 x_{\nu}}{ds^2} \left(\frac{ds}{dx_0} \right)^2 + \frac{dx_{\nu}}{ds} \frac{d^2 s}{dx_0^2} = \frac{d_x dx_{\nu}}{dx_0^2}; \quad \dots \quad (4)$$

especially for $x_{\nu} = x_0$

$$\frac{d^2 x_0}{ds^2} \left(\frac{ds}{dx_0} \right)^2 = - \frac{dx_0}{ds} \frac{d^2 s}{dx_0^2}. \quad \dots \quad (4')$$

If therefore we multiply the former of the equations

$$\begin{aligned} \frac{d^2 x_{\nu}}{ds^2} + \sum_{\lambda, \mu} \left\{ \begin{smallmatrix} \lambda & \mu \\ \nu \end{smallmatrix} \right\} \frac{dx_{\lambda}}{ds} \frac{dx_{\mu}}{ds} &= 0 \\ \frac{d^2 x_0}{ds^2} + \sum_{\lambda, \mu} \left\{ \begin{smallmatrix} \lambda & \mu \\ 0 \end{smallmatrix} \right\} \frac{dx_{\lambda}}{ds} \frac{dx_{\mu}}{ds} &= 0 \end{aligned}$$

by $\left(\frac{ds}{dx_0} \right)^2$, the latter by $\left(\frac{ds}{dx_0} \right)^2 \frac{dx_{\nu}}{dx_0}$, we find after subtraction by the aid of (4) and (4')

$$\frac{d^2 x_{\nu}}{dx_0^2} + \sum_{\lambda, \mu} \left[\left\{ \begin{smallmatrix} \lambda & \mu \\ \nu \end{smallmatrix} \right\} - \left\{ \begin{smallmatrix} \lambda & \mu \\ 0 \end{smallmatrix} \right\} \frac{dx_{\nu}}{dx_0} \right] \frac{dx_{\lambda}}{dx_0} \frac{dx_{\mu}}{dx_0} = 0. \quad \dots \quad (5)$$

These are the equations of the geodesic which we had in view. Taken as the equations of the geodesic of a two-dimensional space (a surface in the usual meaning), they give

$$\begin{aligned} \frac{d^2 v}{du^2} - \left\{ \begin{smallmatrix} 2 & 2 \\ 1 \end{smallmatrix} \right\} \left(\frac{dv}{du} \right)^2 + \left(\left\{ \begin{smallmatrix} 2 & 2 \\ 2 \end{smallmatrix} \right\} - 2 \left\{ \begin{smallmatrix} 1 & 2 \\ 1 \end{smallmatrix} \right\} \right) \left(\frac{dv}{du} \right)^2 + \\ + \left(2 \left\{ \begin{smallmatrix} 1 & 2 \\ 1 \end{smallmatrix} \right\} - \left\{ \begin{smallmatrix} 1 & 1 \\ 1 \end{smallmatrix} \right\} \right) \frac{dv}{du} + \left\{ \begin{smallmatrix} 1 & 1 \\ 2 \end{smallmatrix} \right\} &= 0, \end{aligned}$$

a well known form, which is often taken as the starting point for the discussion of the properties of this line.

§ 2. We multiply (5) by $g_{\nu\rho} \frac{dx_\rho}{dx_\bullet}$ and sum with respect to ν and ρ ; the equation thus found

$$\sum_{\nu,\rho} g_{\nu\rho} \left(\frac{d^2 x_\nu}{dx_\bullet^2} + \sum_{\lambda,\mu,\nu,\rho} g_{\nu\rho} \left[\left\{ \begin{matrix} \lambda & \mu \\ & \nu \end{matrix} \right\} - \left\{ \begin{matrix} \lambda & \mu \\ 0 & \end{matrix} \right\} \frac{dx_\nu}{dx_\bullet} \right] \frac{dx_\lambda}{dx_\bullet} \frac{dx_\mu}{dx_\bullet} \right) \frac{dx_\rho}{dx_\bullet} = 0 \quad (6)$$

may be reduced to a different form.

Let us consider the first term:

$$\sum_{\nu,\rho} g_{\nu\rho} \frac{d^2 x_\nu}{dx_\bullet^2} \frac{dx_\rho}{dx_\bullet};$$

As $g_{\nu\rho} = g_{\rho\nu}$ we may also write this

$$\frac{1}{2} \sum_{\nu,\rho} g_{\nu\rho} \left(\frac{d^2 x_\nu}{dx_\bullet^2} \frac{dx_\rho}{dx_\bullet} + \frac{d^2 x_\rho}{dx_\bullet^2} \frac{dx_\nu}{dx_\bullet} \right) = \frac{1}{2} \sum_{\nu,\rho} g_{\nu\rho} \frac{d}{dx_\bullet} \left(\frac{dx_\nu}{dx_\bullet} \frac{dx_\rho}{dx_\bullet} \right).$$

In the second term

$$\sum_{\lambda,\mu,\nu,\rho} g_{\nu\rho} \left\{ \begin{matrix} \lambda & \mu \\ & \nu \end{matrix} \right\} \frac{dx_\lambda}{dx_\bullet} \frac{dx_\mu}{dx_\bullet} \frac{dx_\rho}{dx_\bullet}$$

we replace $\left\{ \begin{matrix} \lambda & \mu \\ & \nu \end{matrix} \right\}$ by its expression between the square brackets and apply a reduction

$$\begin{aligned} \sum_{\lambda,\mu,\nu,\rho,\tau} g_{\nu\rho} g^{\nu\tau} \left[\begin{matrix} \lambda & \mu \\ & \tau \end{matrix} \right] \frac{dx_\lambda}{dx_\bullet} \frac{dx_\mu}{dx_\bullet} \frac{dx_\rho}{dx_\bullet} &= \sum_{\lambda,\mu,\tau} \left(\left[\begin{matrix} \lambda & \mu \\ & \tau \end{matrix} \right] \frac{dx_\lambda}{dx_\bullet} \frac{dx_\mu}{dx_\bullet} \sum_{\nu,\rho} g^{\nu\tau} g_{\nu\rho} \frac{dx_\rho}{dx_\bullet} \right) = \\ &= \sum_{\lambda,\mu,\tau} \left[\begin{matrix} \lambda & \mu \\ & \tau \end{matrix} \right] \frac{dx_\lambda}{dx_\bullet} \frac{dx_\mu}{dx_\bullet} \frac{dx_\tau}{dx_\bullet}, \end{aligned}$$

as

$$\sum_{\nu} g^{\nu\tau} g_{\nu\rho} \begin{cases} \leq 1 & (\text{for } \rho = \tau) \\ \leq 0 & (\text{for } \rho \neq \tau) \end{cases}.$$

According to the meaning of the symbols [], we may replace the expression thus found by

$$\frac{1}{2} \sum_{\lambda,\mu,\tau} \frac{\partial g_{\lambda\mu}}{\partial x_\tau} \frac{dx_\lambda}{dx_\bullet} \frac{dx_\mu}{dx_\bullet} \frac{dx_\tau}{dx_\bullet} = \frac{1}{2} \sum_{\lambda,\mu} \frac{dx_\lambda}{dx_\bullet} \frac{dx_\mu}{dx_\bullet} \frac{dg_{\lambda\mu}}{dx_\bullet}.$$

The two former terms of (6) may therefore be combined to:

$$\frac{1}{2} \frac{d}{dx_\bullet} \sum_{\lambda,\mu} g_{\lambda\mu} \frac{dx_\lambda}{dx_\bullet} \frac{dx_\mu}{dx_\bullet} = \frac{1}{2} \frac{d}{dx_\bullet} \left(\frac{ds}{dx_\bullet} \right).$$

We write the third term

$$\sum_{\lambda,\mu,\nu,\rho} g_{\nu\rho} \left\{ \begin{matrix} \lambda & \mu \\ & \nu \end{matrix} \right\} \frac{dx_\nu}{dx_\bullet} \frac{dx_\lambda}{dx_\bullet} \frac{dx_\mu}{dx_\bullet} \frac{dx_\rho}{dx_\bullet}$$

as

$$\sum_{\lambda, \rho} \left(g_{\lambda \rho} \frac{dx_\lambda}{dx_0} \frac{dx_\rho}{dx_0} \sum_{\lambda, \mu} \begin{Bmatrix} \lambda & \mu \\ 0 & 0 \end{Bmatrix} \frac{dx_\lambda}{dx_0} \frac{dx_\mu}{dx_0} \right) = \left(\frac{ds}{dx_0} \right)^2 \sum_{\lambda, \mu} \begin{Bmatrix} \lambda & \mu \\ 0 & 0 \end{Bmatrix} \frac{dx_\lambda}{dx_0} \frac{dx_\mu}{dx_0},$$

so that (6) is transformed into

$$\frac{1}{2} \frac{d}{dx_0} \left(\frac{ds}{dx_0} \right)^2 + \left(\frac{ds}{dx_0} \right)^2 \sum_{\lambda, \mu} \begin{Bmatrix} \lambda & \mu \\ 0 & 0 \end{Bmatrix} \frac{dx_\lambda}{dx_0} \frac{dx_\mu}{dx_0} = 0 \quad \dots \quad (7)$$

§ 3. Let us now define a line in time space by

$$x_i = \varphi_i(x_0),$$

where we require of the functions φ :

1. that the line defined in this way satisfy the equations of the geodesic;

2. that in a definite point A

$$\left(\frac{ds}{dx_0} \right)_A^2 \equiv \sum_{i,k} \left(g_{ik} \frac{dx_i}{dx_0} \frac{dx_k}{dx_0} \right)_A = 0.$$

Of course we also suppose that the coordinates x_i are defined as uniform continuous functions of x_0 and that also g_{ik} and its derivatives are uniform continuous functions of the coordinates, at least in the region in consideration.

We have in this way taken care that the line defined by (8) is a geodesic and has a null element in A . As it is a geodesic each of its points satisfies (7); each x_i being a function of x_0 , we may conclude that

$$\frac{d}{dx_0} \left(\frac{ds}{dx_0} \right)^2 - \left(\frac{ds}{dx_0} \right)^2 \Phi(x_0) = 0,$$

where Φ is a uniform continuous function of x_0 .

Hence, along each geodesic

$$\left(\frac{ds}{dx_0} \right)_P^2 = \left(\frac{ds}{dx_0} \right)_A^2 e^{\int_{a_0}^{p_0} \Phi(x_0) dx_0}; \quad \dots \quad (8)$$

by a_0 and p_0 we understand the values which x_0 assumes at the starting point A and an arbitrary point P of the line.

However, we have also made the assumption that the geodesic in consideration has a null element in A . Accordingly here

$$\left(\frac{ds}{dx_0} \right)_A^2 = 0.$$

On the other hand there follows from (8) that along this line always

$$\left(\frac{ds}{dx_0} \right)^2 = 0,$$

in other words that the line in consideration is a geodesic null line, which was to be proved.

§ 4. Let x_0 be the time coordinate. In three-dimensional space in a point A an arbitrary direction is defined by giving definite ratios to $\frac{dx_l}{dx_0}$ ($l = 1, 2, 3$). If inversely we assume these ratios as given, we can give such values to $\frac{dx_l}{dx_0}$ that the condition

$$\left(\frac{ds}{dx_0}\right)' \equiv \sum_{\lambda\mu} g_{\lambda\mu} \frac{dx_\lambda}{dx_0} \frac{dx_\mu}{dx_0} = 0 \quad (\lambda, \mu = 0, 1, 2, 3).$$

is satisfied.

The theorem which we have proved, has therefore the meaning:

In three-dimensional space there passes a ray of light at any moment through any point in any direction.

Physics. — "*Calculations of the effective permeability and dielectric constant of a powder.*" By G. BREIT, National Research Fellow U.S.A. (Supplement N°. 46 to the Communications from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated at the meeting of October 28, 1922).

Introductory.

The pure samples of some rare substances are available only in powdered form and show particularly interesting magnetic properties. For this reason it is desirable to know the relation between the measured and the true permeability of a powdered substance.

If the susceptibility is small the effects of the demagnetizing field are negligible and the magnetization of any individual particle of the powder is the same as it would be if the particle were part of a solid block. Supposing that the particles are crystalline, the measured specific susceptibility is the mean specific susceptibility of a crystal provided in taking the mean equal weights are given to all orientations of the crystal.

In the case of gadolinium sulphate at 2° K. the magnetization is considerable and the above approximation does not suffice. This fact has been realized by Prof. H. KAMERLINGH ONNES and a correction has been made by him¹). Prof. KAMERLINGH ONNES expressed his desire to the author to see a more accurate correction. This forms the subject of the following pages.

Approximations and statement of problem.

In view of the random distribution of the principal directions of the individual crystalline particles the difference between susceptibilities in different directions will be neglected. This probably introduces an error in the calculations which however is likely to be small.

It will be supposed that the applied field is so small that the magnetization is proportional to the field. Some of the results of the calculation are independent of this assumption as will be brought out later.

¹) Leiden Comm. Suppl. N°. 44a p. 10.

For convenience of notation the electrostatic problem of a powdered dielectric in an electric field will be treated. The results are translated into the magnetic case by substituting the permeability μ for the dielectric constant ϵ .

Our problem is to calculate the effective dielectric constant of a powder under the above assumptions as to the smallness of the field and the random distribution of the axes when the density of packing of the powder and the dielectric constant of the material of the powder are known.

Definition of "effective dielectric constant".

Let us consider a portion of the powder which contains many particles and let us take the mean electric intensity and the mean electric displacement throughout this portion. (The mean being taken with respect to volume). We define: "effective dielectric constant" =
$$= 4\pi \frac{\text{mean electric displacement}}{\text{mean electric intensity}}.$$

We presuppose that this definition is unique which implies that the powder is sufficiently fine for otherwise it is not possible to include a sufficient number of particles without making the portion so large that the field would vary in it (from point to point) if the powder were replaced by a solid.

Let us draw a spherical surface inside the powder. According to the well known treatment of polarized media the electric intensity inside the sphere is equal to the electric intensity due to charges inside the sphere plus the intensity due to charges of polarization on the surface of the sphere and plus the intensity due to charges of polarization on the outer surface of the powder as well as that due to charges outside and inside the powder. This means that the electric intensity

$$E = E_i + E_p + E_o$$

where

E_i = effect of charges inside the sphere

E_p = effect of charges of polarization on the surface of the sphere

E_o = effect of charges of polarization on the outer surface of the powder + external field

where "external field" = field due to all real charges and the charges of polarization not belonging to the powder.

Since each individual particle is uncharged E_i is obtained by summing the fields due to charges of polarization on the surfaces of the particles inside the sphere.

If \bar{E}_0 should denote the average value of E_0 throughout the sphere we have with a good approximation $\bar{E}_0 = \bar{E}$ because the usual treatment of polarized media may be applied to \bar{E} and the result is E_0 if the powder is fine.

Let a certain volume be occupied by the powder and put in an external field \mathfrak{E} . Then $E_0 \neq \mathfrak{E}$ on account of the charges of polarization on the outer surface of the volume. It is for this fact that the correction has been made by Prof. H. KAMERLINGH ONNES. We shall suppose in what follows that this or an equivalent correction is made in the final interpretation of the experiment. In order to make such a correction however one must first obtain the effective dielectric constant and then operate with this constant just as one would in the case of a homogeneous medium. Thus e.g. it may be shown¹⁾ that the force on a sphere of radius a placed in a field of force given by $E_0 + Bz$ parallel to the OZ axis of a rectangular system of coördinates having its origin at the centre of the sphere and $-\frac{B\rho}{2}$ along the radius ρ perpendicular to the axis of z is $F = a^3 \frac{\epsilon-1}{\epsilon+2} B E_0$ where E_0, B are constants and ϵ is the dielectric constant. Hence

$$\epsilon = \frac{2 F / a^3 B E_0 + 1}{1 - F / a^3 B E_0}$$

Preliminary approximate solutions.

(a) A space lattice of spheres.

Consider a space lattice of spheres the density of packing being not too great. We can get very easily an approximate solution for this case. Let us suppose that each sphere has its boundary removed so far from the surface of the adjacent spheres that the field acting

¹⁾ Using equation (6) (to be derived presently) we find that the density of the fictitious distribution of charge is (using polar coördinates with OZ as axis)

$$\sigma_i = \frac{1}{4\pi} (E_{in_2} - E_{in_1}) = \frac{1}{4\pi} \left[\frac{3(\epsilon-1)}{\epsilon+2} E_0 P_1(\cos \theta) + \frac{5(\epsilon-1)}{2\epsilon+3} B a P_2(\cos \theta) \right].$$

Hence the force

$$F = \int_{\cos \theta = -1}^{+1} \frac{a^3}{2} [E_0 + B a P_1(\cos \theta)] \left[\frac{3(\epsilon-1)}{\epsilon+2} E_0 P_1(\cos \theta) + \frac{5(\epsilon-1)}{2\epsilon+3} B a P_2(\cos \theta) \right] d(\cos \theta) = a^3 \frac{\epsilon-1}{\epsilon+2} E_0 B.$$

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on it may be considered as uniform. Then the sphere is uniformly polarized, the polarization being $\frac{3}{4\pi} \frac{\epsilon_0 - 1}{\epsilon_0 + 2} F$, where ϵ_0 is the dielectric constant of the sphere and F is the uniform field acting on the sphere. If q should denote the fraction of the volume of the lattice which is occupied by the spheres themselves, the average polarization is

$$P = \frac{3q}{4\pi} \frac{\epsilon_0 - 1}{\epsilon_0 + 2} F.$$

Since now the effect of a uniformly polarized sphere at points outside the sphere is equivalent to the effect of a doublet at the centre of the sphere the contribution to F of the particles of powder situated inside the large spherical hole vanishes by a well known reasoning of LORENTZ¹⁾ and his result for F applies here so that

$$F = E + \frac{4\pi}{3} P = E + q \frac{\epsilon_0 - 1}{\epsilon_0 + 2} F$$

i.e.

$$F = \frac{E}{1 - q \frac{\epsilon_0 - 1}{\epsilon_0 + 2}}$$

and

$$P = \frac{3q}{4\pi} \frac{E}{\frac{\epsilon_0 + 2}{\epsilon_0 - 1} - q} = \frac{\epsilon - 1}{4\pi} E$$

where ϵ is the effective dielectric constant.

Thus

$$\frac{\epsilon - 1}{q(\epsilon_0 - 1)} = \frac{1}{\frac{\epsilon_0 + 2}{3} - \frac{q}{3}(\epsilon_0 - 1)} \quad \dots \quad (1)$$

and letting

$$\begin{aligned} p + q &= 1 \\ \epsilon_0 &= 1 + d \quad \dots \quad (1_A) \end{aligned}$$

we have

$$\frac{\epsilon - 1}{q(\epsilon_0 - 1)} = \frac{1}{1 + \frac{pd}{3}} \quad \dots \quad (1')$$

Thus the effective susceptibility of a powder is not proportional

¹⁾ H. A. LORENTZ, Theory of Electrons, p. 308

to the density of packing but should be corrected by the factor $\frac{1}{1+p\delta/3}$.

It is worth noting that (1) may be written as

$$\frac{\epsilon-1}{\epsilon+2} = q \frac{\epsilon_0-1}{\epsilon_0+2} \dots \dots \dots (1'')$$

which means that if the powder is moulded in a sphere then the force on that sphere is a q^{th} part of the force which would be exerted on a solid sphere of the same radius. In other words each individual particle of the powder may be considered as acted on only by the external force. (I have seen a very direct and simple proof of this fact from Prof. EHRENFEST).

We see therefore that to within the approximations made so far the factor $\frac{1}{1 + \frac{4\pi\sigma d}{3H}}$ used by Prof. H. KAMERLINGH ONNES should be

used with the value of the density in the solid — not the powdered form.

(b) *A space lattice of spherical holes*¹⁾.

The case considered above may be expected to give a good approximation if the powder is packed loosely. If it is packed closely a better approximation must be expected from a space lattice of holes.

It is not necessary to treat this case independently because use can be made of formula (1) if it is remembered that in (1) ϵ is the ratio of the effective dielectric constant to the dielectric constant of the space between the spheres of the lattice. Denoting by q as before the proportion of the volume occupied by the substance (i.e. the ratio to the total volume of total volume minus the volume of the holes) and leaving (1_A) unchanged we arrive at

$$\frac{\epsilon-1}{q(\epsilon_0-1)} = \frac{1}{1 + \frac{p\delta}{3+2\sigma}} \dots \dots \dots (2)$$

which may be also shown to be equivalent to

$$\frac{\epsilon-1}{\epsilon_0-1} = \frac{1}{1 + \frac{3\epsilon_0}{1+2\epsilon_0} \frac{p}{q}} \dots \dots \dots (2')$$

¹⁾ The possibilities of this case have been pointed out to me by Prof. H. KAMERLINGH ONNES and Dr. H. R. WOLTJER.

From either of these formulas we find

$$\frac{\epsilon-1}{\epsilon+2} = q \frac{\epsilon_0-1}{\epsilon_0+2 - \frac{2pd^2}{3+2d}} \dots \dots \dots (2'')$$

This formula is analogous to (1'') in (a) and shows that to within the first power of d the force on a sphere having spherical holes in it is the same as if the sphere were moulded into a smaller sphere without holes. Thus the conclusions drawn in (a) for the correction factor

$$\frac{1}{1 + \frac{4\pi\sigma d}{3H}}$$

remain valid in this case.

(c) *Laminary structure of powder the directions of the laminae being distributed statistically. (See fig. 1).*

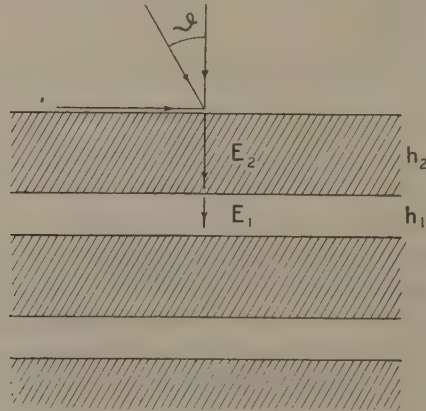


Fig. 1.

The electric intensity may be resolved into two components normal and parallel to the laminae respectively.

(I) Normal component.

Letting E_1 , E_2 , h_1 , h_2 , ϵ_1 , ϵ_2 be respectively the normal components of the field intensity, the thicknesses, and the dielectric constants of the interspaces between the laminae and the laminae themselves we have:

$$\frac{E_1}{\epsilon_1^{-1}} = \frac{E_2}{\epsilon_2^{-1}} = \frac{h_1 E_1 + h_2 E_2}{h_1 \epsilon_1^{-1} + h_2 \epsilon_2^{-1}}.$$

Writing

$$h_1 E_1 + h_2 E_2 = (h_1 + h_2) \bar{E}$$

and letting

$$\frac{\overline{E}}{\epsilon_n^{-1}} = \frac{E_1}{\epsilon_1^{-1}}$$

we obtain

$$\epsilon_n = \frac{h_1 + h_2}{h_1 \epsilon_1^{-1} + h_2 \epsilon_2^{-1}} = \frac{1}{p + q \epsilon_0^{-1}}$$

having let

$$\epsilon_1 = 1, \epsilon_2 = \epsilon_0, \frac{h_2}{h_1 + h_2} = q, \frac{h_1}{h_1 + h_2} = p.$$

This number ϵ_n is the effective dielectric constant for the component normal to the laminae.

(II) Parallel component.

For this it is clear that the effective dielectric constant is

$$\epsilon_p = \frac{h_1 \epsilon_1 + h_2 \epsilon_2}{h_1 + h_2} = p + q \epsilon_0$$

(III) Both components present.

The electric displacement is $\frac{E}{4\pi} (\epsilon_n \cos \vartheta, \epsilon_p \sin \vartheta)$ where ϑ is the angle made by the mean electric intensity with the normal to the laminae. Since the directions of the normals to the laminae are entirely arbitrary with respect to the direction of the mean electric intensity, the component of the electric displacement perpendicular to the mean electric intensity is distributed at random. The only component to be considered is then that parallel to the mean electric intensity which is $\frac{E}{4\pi} (\epsilon_n \cos^2 \vartheta + \epsilon_p \sin^2 \vartheta)$. The effective dielectric constant is

$$\epsilon = \epsilon_n \overline{\cos^2 \vartheta} + \epsilon_p \overline{\sin^2 \vartheta} = \frac{\epsilon_n + 2 \epsilon_p}{3}$$

Hence we get

$$\frac{\epsilon - 1}{q(\epsilon_0 - 1)} = \frac{1 + \frac{2}{3} p \sigma}{1 + p \sigma} \quad \dots \quad (3)$$

To within the first power of σ this is the same as (2) or (1') so that in this case the conclusions drawn as to a force on a sphere are still valid. Rewriting (3) in the form

$$\frac{\epsilon - 1}{q(\epsilon_0 - 1)} = \frac{1}{1 + \frac{p \sigma}{3 + 2 p \sigma}} \quad \dots \quad (3')$$

it becomes apparent that the value of ϵ obtained from (3) lies between the values obtained from (1') and (2).

Variable susceptibility.

To within the approximations made so far the case of variable susceptibility offers no difficulty. Thus in the case (a) it was assumed that the field acting on each particle of the powder is uniform. Whether the susceptibility of this particle depends on the field or not its polarization is uniform and is such that the electric intensity E inside the particle is

$$E = \frac{3}{\epsilon_0(E) + 2} F$$

where F is the intensity of the field acting on the particle and $\epsilon_0(E)$ is the value of the dielectric constant of the material of the particle corresponding to E . If the mean field is \bar{E} , $F = \bar{E} + \frac{4\pi}{3} P$ and $P = q \frac{\epsilon_0(E) - 1}{4\pi} E$. Hence E and ϵ_0 are the result of solving the simultaneous equations

$$\left(\epsilon_0 + \frac{3}{p} - 1 \right) E = \frac{3}{p} \bar{E} \Bigg\} \\ \epsilon_0 = \epsilon_0(E)$$

The solution may be obtained graphically or otherwise.

In the calculations that follow the correction for variable susceptibility is more complex and will not be considered.

The distribution of potential in a rectangular space lattice of dielectric spheres.

In order to investigate the errors involved in the approximations we shall look for an exact solution in the case of a space lattice of dielectric spheres. The following notation will be employed:

h = distance between centres of adjacent spheres.

ϵ_0 = dielectric constant of the material of the spheres.

(r, ϑ, φ) = polar coördinates of a point referred to centre of sphere placed at the origin. The polar axis is chosen along one of the rectangular axes of the lattice.

$(r_1, \vartheta_1, \varphi_1)$ = polar coördinates of a point referred to centre of sphere whose Cartesian coördinates are:

(x_1, y_1, z_1) and whose polar coördinates are:

(R_1, Θ_1, Φ_1) .

The radius of each sphere is taken to be 1. The mean field is also supposed to be 1 and directed along the polar axis.

Polarization of single sphere in external field.

Before proceeding with the solution of the problem it will be convenient to derive an expression for the state of polarization of a dielectric sphere placed in a known external field. Charges of polarization are induced. If the electric intensity due to these charges be E_i and if the impressed electric intensity be E_e , the total intensity is $E = E_e + E_i$. Let us suppose that E_i may be derived from a potential

$$V = \sum_{n,m} \frac{A_n^m P_n^m(\cos \vartheta) \cos m\varphi}{r^{n+1}} \quad \dots \quad (4)$$

outside the sphere. Then it must be derivable from

$$V = \sum_{n,m} A_n^m r^n P_n^m(\cos \vartheta) \cos m\varphi \quad \dots \quad (5)$$

inside the sphere since the potential is continuous at the surface. Denoting the components along the outward drawn normal by the suffix n and referring to the state just inside the sphere by n_1 and to the state just outside by n_2 we have the boundary condition

$$\epsilon_0 (E_{en} + E_{in_1}) = E_{en} + E_{in_2}$$

or

$$(\epsilon_0 - 1) E_{en} = E_{in_2} - \epsilon_0 E_{in_1}$$

Using (4) and (5)

$$(\epsilon_0 - 1) E_{en} = \sum_{n,m} (n\epsilon_0 + n + 1) A_n^m P_n^m(\cos \vartheta) \cos m\varphi \quad \dots \quad (6)$$

Thus if E_{en} can be expanded in a series of surface harmonics the coefficients A_n^m may be determined from (6) and hence the state of polarization of the sphere may be obtained.

Derivation of expansion for E_{en} .

In order to solve the problem it will be sufficient to express E_{en} in terms of A_n^m and substitute the result in (6).

The average polarization of the medium being $\frac{A_1^0}{h^3}$ we have

$$E_{en} = \left(1 + \frac{4\pi A_1^0}{3 h^3}\right) \cos \vartheta - \frac{\partial}{\partial r} \left(\sum_1' \sum_{n,m} \frac{A_n^m P_n^m(\cos \vartheta_1) \cos m\varphi_1}{r_1^{n+1}} \right)_{r=1}$$

the first summation being extended over all the spheres inside a large sphere having its centre at the origin, the dielectric sphere situated at the origin being omitted from the summation as indicated by the accent. Using the notation:

$$D_{(c)}^m = \frac{\partial^{n-m}}{\partial x^{n-m}} D_{(c)}^m$$

$$D_c^m = \frac{\partial^m}{\partial \xi^m} + \frac{\partial^m}{\partial \eta^m}$$

$$\xi = x + i y, \quad \eta = x - i y$$

and letting

$$b_0 = 1; \quad b_1, b_2, \dots = \frac{1}{2}$$

it may be shown that [see appendix formula (1_A)]

$$\frac{\cos m \varphi_1 P_n^m(\cos \vartheta_1)}{r_1^{n+1}} = \frac{(-)^n 2^m b_m}{(n-m)!} D_{(c)}^m \left(\frac{1}{r_1} \right) \dots \quad (7)$$

the differentiation being performed with respect to the end point of the vector r_1 i.e. with respect to (r, ϑ, φ) . Thus

$$E_{en} = \left(1 + \frac{4\pi A_1^0}{3 h^3} \right) \cos \vartheta - \frac{\partial}{\partial r} \left(\sum_{m,n=1,\dots} \frac{(-)^n 2^m b_m A_n^m}{(n-m)!} D_{(c)}^m \sum_1' \left(\frac{1}{r_1} - \frac{1}{R_1} \right) \right)_{r=1}$$

where $\frac{1}{R_1}$ has been subtracted from $\frac{1}{r_1}$ so as to secure absolute convergence of expansions that follow. Now

$$\frac{1}{r_1} - \frac{1}{R_1} = \sum_{n=1}^{\infty} \frac{r^n}{R_1^{n+1} b_m(n+m)!} P_n^m(\cos \vartheta) P_n^m(\cos \Theta_1) \cos m(\varphi - \Phi_1).$$

When this is summed with respect to R_1, Θ_1, Φ_1 terms in $\sin m \Phi_1$ and all terms with an odd m drop out. Hence

$$E_{en} = \left(1 + \frac{4\pi A_1^0}{3 h^3} \right) \cos \vartheta - \frac{\partial}{\partial r} \left(\sum_{m,n} \frac{(-)^n 2^m b_m A_n^m}{(n-m)!} \sum_{\nu,\mu} r^\nu P_\nu^\mu(\cos \vartheta) \cos \mu \varphi \frac{S_\nu^\mu}{b_\mu} \right)_{r=1}$$

where

$$S_\nu^\mu = \sum' \frac{(v-\mu)! P_\nu^\mu(\cos \Theta_1) \cos \mu \Phi_1}{(v+\mu)! R_1^{v+1}} \dots \quad (8)$$

Now it may be shown that [see Appendix formula (2_A)]

$$D_{(c)}^m \left(\frac{r^\nu P_\nu^\mu(\cos \vartheta) \cos \mu \varphi}{b_\mu} \right) = \frac{(-)^m}{2^m} \frac{(v+\mu)!}{(v+\mu-n+m)!} \frac{r^{v-n} P_{v-n}^{\mu+m}(\cos \vartheta) \cos(m+\mu) \varphi}{b_{m+\mu}}$$

which when substituted into the expression for E_{en} just found gives:

$$E_{en} = \left(1 + \frac{4\pi A_1^0}{3 h^3} \right) P_1(\cos \vartheta) - \left. \begin{aligned} & - \sum (-)^{n+m} \frac{b_m}{b_{m+\mu}} \frac{(v+\mu)! (v-n) A_n^m S_\nu^\mu P_{v-n}^{\mu+m}(\cos \vartheta) \cos(m+\mu) \varphi}{(n-m)! (v+\mu-n+m)!} = \\ & = \sum_{n,m} \frac{(n\epsilon_0 + n + 1) A_n^m P_n^m(\cos \vartheta) \cos m \varphi}{\epsilon_0 - 1} \end{aligned} \right\} \quad (9)$$

in virtue of (6). Equating coefficients of P_1 we have

$$\left(\frac{\epsilon_0 + 2}{\epsilon_0 - 1} - \frac{4\pi}{3h^3} \right) A_1^0 = 1 + 4A_3^0 S_4^0 + 6A_5^0 S_6^0 + \dots \quad (10)$$

where use is made of the fact that $S_2^0 = \sum' \frac{\frac{3}{2} \cos^2 \theta_1 - \frac{1}{2}}{R_1^3} = 0$. In order to obtain $A_1^{(0)}$ we are thus in need of A_3^0, A_5^0 , etc. For these it follows from (9) that

$$\frac{[(2s+1)\epsilon_0 + 2s+2] A_{2s+1}}{\epsilon_0 - 1} = \sum_{p=0,1,\dots}^{\infty} \frac{(2s+2p+2)! S_{2s+2p+2}}{(2s)!(2p+1)!} A_{2p+1} \quad (s=1, 2, 3, \dots)$$

the upper subscript being dropped for the present. Writing

$$\beta_s = \frac{\epsilon_0 - 1}{\epsilon_0 + \frac{2s+2}{2s+1}}; \quad \alpha_s = \frac{A_{2s+1}}{A_1}; \quad (s, p) = \frac{(2s+2p+2)!}{(2s+1)!(2p+1)!} \quad (11)$$

$$S_{2p+2s+2} = \sigma_{p+s}$$

we have

$$\alpha_s = \beta_s \sum_{p=0}^{\infty} (s, p) \sigma_{p+s} \alpha_p, \quad (s=1, 2, 3, \dots) \quad (12)$$

or

$$\alpha_s = \beta_s (s, 0) \sigma_s + \beta_s \sum_{p=1}^{\infty} (s, p) \sigma_{p+s} \alpha_p \quad (12')$$

Substituting for α_p on the right hand side the expression which follows for it from (12') and proceeding in this manner indefinitely we obtain purely symbolically on changing suffixes:

$$\begin{aligned} \alpha_s = & \beta_s (s, 0) \sigma_s + \sum_{s_1=1}^{\infty} \beta_s \beta_{s_1} (s, s_1) (s_1, 0) \sigma_{s+s_1} + \\ & + \sum_{s_1, s_2=1}^{\infty} \beta_s \beta_{s_1} \beta_{s_2} (s, s_1) (s_1, s_2) (s_2, 0) \sigma_{s+s_1+s_2} + \dots \\ & + \sum_{s_1, s_2, s_3, \dots=1}^{\infty} \beta_s \beta_{s_1} \dots \beta_{s_p} (s, s_1) (s_1, s_2) \dots (s_{p-1}, s_p) (s_p, 0) \sigma_{s+s_1+s_2+\dots+s_{p-1}+s_p} + \dots \end{aligned}$$

where

$$\sigma_{x,y,z,\dots} = \sigma_x \sigma_y \sigma_z \dots \quad (13)$$

If the spacing of the lattice is large in comparison with the diameter of each sphere this expansion may be expected to converge rapidly. As a first approximation the first term will suffice giving

$$\alpha_s = (2s+2) \beta_s \sigma_s \quad (13')$$

Using (10) and (11) we have for the average polarization $P = A_1 h^{-3}$ and the effective dielectric constant ϵ

$$\epsilon - 1 = 4\pi P = \frac{3q}{\frac{\epsilon_0 + 2}{\epsilon_0 - 1} - q - \sum_1^{\infty} (2s + 2) \alpha_s \sigma_s} \quad . \quad . \quad (14)$$

where $q = \frac{4\pi}{3} h^{-3}$ and denotes as before the proportion of the total space occupied by the material of dielectric constant ϵ_0 .

So far we have considered the field only in the direction of one of the axes of the lattice. If the lattice is rectangular and not cubical the quantities σ_s may be different for the three principal directions. In the case of a cubical lattice however they are the same. Since all the relations of the problem are linear the effective dielectric constant in a cubical lattice is independent of the direction of the field and may be thus justly compared with the effective dielectric constant of a powder.

If the first approximation (13') is substituted for α_s into (14) the approximate formula

$$\epsilon - 1 = \frac{3q}{\frac{\epsilon_0 + 2}{\epsilon_0 - 1} - q - \sum_1^{\infty} (2s + 2)^2 \beta_s \sigma_s^2} \quad . \quad . \quad . \quad (14')$$

is obtained. In the summation of this formula the density of packing enters through the quantities σ_s and the intensity of polarization comes in through β_s . The quantity $\epsilon_0 - 1$ occurs in these to the first power. If the more accurate formula (13) were used higher powers of $\epsilon_0 - 1$ would come in. Hence if the density of packing is kept constant and if deviations from the simple formula (1'') just become apparent due to an increase in ϵ_0 formula (14') is the proper one to use. On using (11) it may be simplified to

$$\epsilon - 1 = \frac{3q}{\frac{\epsilon_0 + 2}{\epsilon_0 - 1} - q - (\epsilon_0 - 1) \sum_1^{\infty} \frac{2s + 1}{4s + 3} (2s + 2)^2 \bar{\sigma}_s^2 \left(\frac{6q}{\pi} \right)^{\frac{4s}{3} + 2}} \quad (14'')$$

where $\bar{\sigma}_s$ is the value of σ_s for $q = \frac{\pi}{6}$ which is the maximum possible q for the lattice. The quantities $\bar{\sigma}_s$ are rapidly diminishing as s increases. Thus we find

$$\frac{3}{7} (4\bar{\sigma}_1)^2 = 0.0646, \quad \frac{5}{11} (6\bar{\sigma}_2)^2 = 0.00032.$$

Writing

$$q' = \sum_1^{\infty} \frac{2s + 1}{4s + 3} (2s + 2)^2 \bar{\sigma}_s^2 \left(\frac{6q}{\pi} \right)^{\frac{4s}{3} + 2} \quad . \quad . \quad . \quad (15)$$

we get on neglecting terms of higher order than the second in $\epsilon_0 - 1$

$$\frac{\epsilon - 1}{\epsilon + 2} = q \frac{\epsilon_0 - 1}{\epsilon_0 + 2} \left[1 + \frac{(\epsilon_0 - 1)^2}{3} q' \right] \dots \dots \dots (16)$$

Thus owing to the interaction among the particles of the powder the force on a ball made of the powder can no longer be considered as the sum of the forces on the individual particles independently. The increase of the force to within terms in $(\epsilon_0 - 1)^2$ is given by the factor $1 + \frac{(\epsilon_0 - 1)^2}{3} q'$. For the maximum possible value of q for the model considered $q' = 0.065$ and the correction factor becomes $1 + \frac{(\epsilon_0 - 1)^2}{46}$. If the quantity $\frac{4\pi \sigma d}{3 H}$ of Suppl. N^o. 44a is 0.09 for gadolinium sulphate at 2° K. then since d was taken as $\frac{3}{4}$ of the actual density the quantity $\epsilon_0 - 1$ becomes 0.36 and the correction factor is 1.0028. Thus the effect discussed must be taken into account if the measurements of the force are made to within 0.3%. If such a correction is made it should be also borne in mind that even the simple formula (1'') involves terms of the second order in the apparent $(\epsilon - 1)$ if it is solved for ϵ_0 , as may be seen in the following way.

For small values of $\epsilon_0 - 1$ we have $q(\epsilon_0 - 1) = \kappa F$ where F is the force and κ is a constant of the apparatus. For larger values of $\epsilon - 1$ this is not true but it is convenient to call the quantity $\epsilon_a - 1$ defined by the above equation: "the apparent $\epsilon - 1$ ". If the sample is spherical and if the powder may be considered as the cubical lattice just discussed

$$q \frac{\epsilon_0 - 1}{\epsilon_0 + 2} \frac{1}{1 - \frac{(\epsilon_0 - 1)^2}{3} q'} = \frac{\kappa}{3} F = q \frac{\epsilon_a - 1}{3}.$$

Hence

$$\epsilon_0 - 1 = \frac{\epsilon_a - 1}{1 - \frac{\epsilon_a - 1}{3} + \frac{q'}{3} (\epsilon_a - 1)^2} = \left[1 + \frac{\epsilon_a - 1}{3} + \left(\frac{1}{q} - \frac{q'}{3} \right) (\epsilon_a - 1)^2 \right] (\epsilon_a - 1) \quad (17)$$

Thus $\frac{q'}{3}$ occurs here together with the larger term $\frac{1}{q}$.

If the demagnetizing field is negligible as in the case of a thin long tube $\epsilon - 1 = \kappa F = q(\epsilon_a - 1)$ where ϵ is the effective susceptibility. Hence by (14'')

$$\epsilon_0 - 1 = \frac{\epsilon_a - 1}{1 - \frac{p}{3} (\epsilon_a - 1) + \frac{q'}{3} (\epsilon_a - 1)^2} \dots \dots \dots (17')$$

If the sample has the form of a thin slab normal to the lines of force

$$\epsilon_a - 1 = \frac{\epsilon_a - 1}{1 - \frac{1+2q}{3}(\epsilon_a - 1) + \frac{q'}{3}(\epsilon_a - 1)^2} \quad \dots \quad (17'')$$

Space lattice of spherical holes.

From (14'') we get for this case to within the second power of $(\epsilon_0 - 1)^2$

$$\epsilon - 1 = \frac{q(\epsilon_0 - 1)}{1 + \frac{p}{3}(\epsilon_0 - 1) - p\left(\frac{2}{9} - \frac{p'}{3q}\right)(\epsilon_0 - 1)^2}$$

where p' is the same function of h as q' . The corresponding formula for the space lattice of spheres is

$$\epsilon - 1 = \frac{q(\epsilon_0 - 1)}{1 + \frac{p}{3}(\epsilon_0 - 1) - \frac{q'}{3}(\epsilon_0 - 1)^2}$$

The term $\frac{p'}{3q}$ thus tends to reconcile the two expressions. However for the case of touching spheres or touching holes the space lattice of holes has a higher ϵ than the space lattice of spheres even though q is made the same for both. This means that the continuous path of the flux between the holes contributes to a high value of the effective ϵ . It thus becomes apparent that q and ϵ_0 alone do not suffice to determine ϵ even if the structure is on the average isotropic. The correction in $(\epsilon_0 - 1)^2$ may therefore be never applied with certainty and an estimate of its amount is all that the present theory can offer.

SUMMARY.

1. The consideration of the effects of the demagnetizing field for various models of the powder shows that to within the first order terms the correction is the same for all models considered and may be expressed by the fact that the force on a sphere of the powder is equal to the force which would be exerted on the material if it were moulded into a solid sphere instead of being powdered.

2. Different models give results differing in the second order terms in the demagnetizing field.

APPENDIX.

1. It is shown in MAXWELL'S Treatise that

$$Y_c^{(m)} = \frac{(-)^n}{n!} r^{n+1} D_c^m \frac{1}{r}.$$

Now

$$Y_c^m = \frac{2n!}{2^{n+m}(n!)^2} \Theta_n^m \cdot 2 \cos m \Phi$$

and

$$P_n^m = \frac{2n!}{2^n (n-m)! n!} \Theta_n^m.$$

Hence

$$\frac{2 P_n^m (\cos \vartheta) \cos m \Phi}{r^{n+1}} = \frac{(-)^n 2^m}{(n-m)!} D_c^m \frac{1}{r}.$$

It is also well known that

$$\frac{P_n}{r^{n+1}} = \frac{(-)^n}{n!} \frac{\partial^n \left(\frac{1}{r} \right)}{\partial z^n}.$$

These two equations may be combined in:

$$\frac{\cos m \Phi P_n^m (\cos \vartheta)}{r^{n+1}} = \frac{(-)^n 2^m b_m}{(n-m)!} D_c^m \left(\frac{1}{r} \right) \quad . \quad . \quad . \quad (1A)$$

where

$$b_0 = 1; \quad b_1 = b_2 = \dots = \frac{1}{2}.$$

2. To show that:

$$D_c^m \left(\frac{r^\nu P_\nu^\mu (\cos \vartheta) \cos \mu \Phi}{b_\mu} \right) = \frac{(-)^m (v+\mu)! r^{\nu-n} P_\nu^{\mu+m} (\cos \vartheta) \cos (m+\mu) \Phi}{2^m (v+\mu-n+m)! b_{m+\mu}} \quad (2A)$$

We consider the following cases:

$$(I). \quad \mu = m = 0$$

We must show that

$$\frac{\partial^n}{\partial z^n} (r^\nu P_\nu (\cos \vartheta)) = \frac{v! r^{\nu-n}}{(v-n)!} P_{v-n} (\cos \vartheta).$$

Proof. Using LAPLACE'S integral

$$P_\nu (\cos \vartheta) = \frac{1}{\pi} \int_0^\pi (\cos \vartheta + i \sin \vartheta \cdot \cos \Phi)^\nu d\Phi$$

$$\text{we have } r^\nu P_\nu (\cos \vartheta) = \frac{1}{\pi} \int_0^\pi (z + i \varrho \cos \Phi)^\nu d\Phi \text{ where } \varrho = \sqrt{x^2 + y^2},$$

whence the formula follows on differentiation.

$$(II). \quad n = m, \quad \mu = 0$$

We must show that:

$$D_c^m (r^n P_n (\cos \vartheta)) = \frac{(-)^m}{2^m} r^{n-m} P_{n-m}^m (\cos \vartheta) \cdot 2 \cos m\varphi$$

Proof. Since $\varrho^2 = \xi\eta$ we have

$$r^n P_n = \sum_p \frac{(-)^p n! z^{n-2p} \xi^p \eta^p}{2^{2p} (p!)^2 (n-2p)!}$$

Operating on this with D_c^m and observing that

$$P_{n-m}^m (\cos \vartheta) = \frac{n!}{2^m} \sin^m \vartheta \sum_p \frac{(-)^p \cos^{n-2m-2p} \vartheta \sin^{2p} \vartheta}{(n-2m-2p)! 2^{2p} p! (m+p)!}$$

the above written formula follows. An analogous formula holds of course for the operator D_s^m .

$$(III). \quad m \neq 0, \quad \mu \geq 1$$

Using (1_A) and (II), (2_A) is found.

$$(IV). \quad m = 0$$

This is also verified without difficulty.

Physics. — “*On the Heat of Mixing of Normal and Associating Liquids.*” By Dr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

(Communicated at the meeting of September 30, 1922).

1. In connection with a study by J. R. KATZ (published in „Verlag der Wis- en Naturk. Afdeeling Kon. Akad. v. Wetensch.” Vol. XXXI, nos 5/6, p. 333—336) I wish to make a few remarks on the heat of mixing of liquids, also in reference to the quantity a/v^2 (or a/b^2).

Different authors, among others VAN DER WAALS and myself, made use of approximations some time ago, which seemed permissible; but which gave no account, not even in approximation, of the heat-effect, which is sometimes very slight, especially for normal substances. For here the case presented itself that the neglected quantities $((v-b)^2$ by the side of v^2 , p by that of a/v^2) would give a term of higher order of magnitude in the results than that which results from the not neglected part. The latter term appears to be of the order of magnitude $(b_1\sqrt{a_1}-b_1\sqrt{a_2})^2$, whereas that of the neglected part — yielding a term with $(p + a/v^2) \Delta v$ — is of the order $b_1\sqrt{a_1}-b_1\sqrt{a_2}$ on account of Δv ; hence, when the difference of the critical pressures of the components is small, the neglected part will have a much greater value than the not neglected part.

And besides: While the first part — referring to the change of the potential energy without reference to the contraction — will always be *positive*, the second (neglected) part — which is in connection with the *volume contraction* Δv — is nearly always *negative*. In “quasi-ideal” mixtures of two liquids (i.e. liquids the critical pressures of which are about equal), the effect will nearly always be *negative* (i.e. heat is *liberated*), and not *positive*, as the earlier theoretical derivation indicated. In liquids the critical pressures of which are not about equal, sometimes differ even considerably, it will entirely depend on circumstances (relation of the a 's and b 's inter se, value of the mixing ratio x) whether the result will be positive or negative.

In associated components, where Δv can become much greater than in mixtures of normal components (generally the critical pressures also differ much more from each other), the above ratios will

be more greatly accentuated, and the negative term with $(p + a/v_2)\Delta v$ will predominate still more.

Already BAKHUIS ROOZEBOOM — now about twenty years ago — drew my attention to the insufficiency of the approximative expression, but at the time we attributed this to other causes¹⁾, thinking that — especially in quasi-ideal mixtures — the possible volume-contraction would probably be quite negligible. Not until 1912, when in a letter my friend Prof. KREMANN at Graz put a question to me on this subject, was I led to carry out the perfectly accurate calculation of the quantity Δv ²⁾.

In what follows I may be allowed to give the exact theory, first of all of mixtures of normal components. Here too the perfectly accurate derivation appears to be by no means more difficult or longer than the approximated derivation, and the result is almost equally simple. The same thing is found here as before with the exact derivation of the equations of the spinodal and the plaitpoint line³⁾. There the perfectly accurate results are even simpler than the earlier approximated expressions.

2. Heat of mixing of normal components.

From the well-known expression for the total energy

$$e = e' + kT - \frac{a}{v} + pv,$$

in which the energy constant e' is $= n_1 e'_1 + n_2 e'_2$, and the heat capacity at constant (infinitely great) volume $k = n_1 k_1 + n_2 k_2$, we find for the pure components:

$$\left. \begin{aligned} e_1^* &= e'_1 + k_1 T - \frac{a_1}{v_1^*} + p v_1^* \\ e_2^* &= e'_2 + k_2 T - \frac{a_2}{v_2^*} + p v_2^* \end{aligned} \right\}.$$

For the *integral* heat of mixing of n_1 gr. mol. of one component and n_2 gr. mol. of the other component the expression

¹⁾ Inaccuracy of VAN DER WAALS' equation of state; non-validity of BERTHELOT's assumption $a_{12} = \sqrt{a_1 a_2}$, etc. But since then I have got more than ever convinced of the absolute validity (in liquids) of the said equation and B's assumption. Of course a and b then have *other* values than in the gaseous state, but this need, of course, not be considered here.

²⁾ Later inserted summarized in his valuable — unfortunately too little known — book: "Die Eigenschaften der binären Flüssigkeitsgemische etc." (Sammlung (HERZ) chemischer Vorträge Bd. 23, Stuttgart, Enke, 1916); see p. 170—171.

³⁾ These Proc. Vol. VII, p. 646; Vol. VIII, p. 33.

$$w = - \left(\frac{a}{v} - n_1 \frac{a_1}{v_1^0} - n_2 \frac{a_2}{v_2^0} \right) + p (v - n_1 v_1^0 - n_2 v_2^0) \quad . \quad . \quad (a)$$

is at once found from

$$w = e - (n_1 e_1^0 + n_2 e_2^0)$$

Now

$$\frac{a}{v} = \frac{a}{v_0} + \left(\frac{a}{v} - \frac{a}{v_0} \right) = \frac{a}{v_0} - \frac{a}{v v_0} \Delta v,$$

in which $v_0 = n_1 v_1^0 + n_2 v_2^0$, and $v - v_0 = \Delta$ is written. Further $a = (n_1 \sqrt{a_1} + n_2 \sqrt{a_2})^2$, and from this follows:

$$\frac{a}{v_0} = \left(n_1 \frac{a_1}{v_1^0} + n_2 \frac{a_2}{v_2^0} \right) - n_1 n_2 \frac{(v_2^0 \sqrt{a_1} - v_1^0 \sqrt{a_2})^2}{v_0 v_1^0 v_2^0}.$$

Hence:

$$w = n_1 n_2 \frac{(v_2^0 \sqrt{a_1} - v_1^0 \sqrt{a_2})^2}{v_0 v_1^0 v_2^0} + \left(p + \frac{a}{v v_0} \right) \Delta v \quad . \quad . \quad (1)$$

Remarks. a. Formerly ¹⁾ the following equation was written:

$$\frac{a}{v} = \frac{a}{v} + \left(\frac{a}{v^2} (v-b) + p(v-b) - (n_1 + n_2) RT \right),$$

on account of the equation of state. This gives:

$$\begin{aligned} \frac{a}{v} &= \frac{a}{v^2} (2v-b) + p(v-b) - (n_1 + n_2) RT = \frac{a}{b} \left(1 - \left(\frac{v-b}{v} \right)^2 \right) + \\ &+ p(v-b) - (n_1 + n_2) RT, \end{aligned}$$

hence:

$$e = e' + \left(k + (n_1 + n_2) R \right) T - \frac{a}{b} \left(1 - \frac{(v-b)^2}{v^2} \right) + p b,$$

for which $e = e' + k' T - a/b$ was written — with an apparently perfectly justifiable neglect of some terms. Then we get:

$$w = n_1 n_2 \frac{(b_2 \sqrt{a_1} - b_1 \sqrt{a_2})^2}{b b_1 b_2}.$$

It is seen that the very essential term $\frac{a}{v v_0} \Delta v$ is omitted.

b. We might also have written:

$$\frac{a}{v} = n_1 \frac{a_1}{v_1} + n_2 \frac{a_2}{v_2} - n_1 n_2 \frac{(v_2 \sqrt{a_1} - v_1 \sqrt{a_2})^2}{v v_1 v_2},$$

in which $v_1 = \frac{\partial v}{\partial n_1}$ and $v_2 = \frac{\partial v}{\partial n_2}$. For according to a property of the

¹⁾ Cf. among others Zeitschr. f. physik. Ch. 63, p. 219 (1908).

homogeneous functions of the first degree with regard to n_1 and n_2 , we have $v = n_1 v_1 + n_2 v_2$. And further according to (a):

$$w = n_1 n_2 \frac{(v_2 \sqrt{a_1 - v_1 \sqrt{a_2}})^2}{v v_1 v_2} + n_1 \left(\frac{a_1}{v_1^0} - \frac{a_1}{v_1} \right) + n_2 \left(\frac{a_2}{v_2^0} - \frac{a_2}{v_2} \right) + p (n_1 (v_1 - v_1^0) + n_2 (v_2 - v_2^0)),$$

or also

$$w = n_1 n_2 \frac{(v_2 \sqrt{a_1 - v_1 \sqrt{a_2}})^2}{v v_1 v_2} + \left(p + \frac{a_1}{v_1 v_1^0} \right) n_1 \Delta v_1 + \left(p + \frac{a_2}{v_2 v_2^0} \right) n_2 \Delta v_2, \quad (1^a)$$

which expression will at once appear to be useful.

Here is $v_1 - v_1^0 = \Delta v_1$ and $v_2 - v_2^0 = \Delta v_2$, and evidently we have $\Delta v = v - v_0 = (n_1 v_1 + n_2 v_2) - (n_1 v_1^0 + n_2 v_2^0) = n_1 \Delta v_1 + n_2 \Delta v_2$.

For the differential heats of mixing $w_1 = \frac{\partial w}{\partial n_1}$ and $w_2 = \frac{\partial w}{\partial n_2}$ we now have from $(1^a)^1$:

$$w_1 = n_2 \frac{(v_2 \sqrt{a_1 - v_1 \sqrt{a_2}})^2}{v_1 v_2} \frac{\partial}{\partial n_1} \left(\frac{n_1}{v} \right) + \left(p + \frac{a_1}{v_1 v_1^0} \right) \Delta v_1,$$

$$\text{or as } \frac{\partial}{\partial n_1} \left(\frac{n_1}{v} \right) = \frac{v - n_1 v_1}{v^2} = \frac{n_2 v_2}{v^2}:$$

$$w_1 = n_2 \frac{(v_2 \sqrt{a_1 - v_1 \sqrt{a_2}})^2}{v^2 v_1} + \left(p + \frac{a_1}{v_1 v_1^0} \right) \Delta v_1$$

Likewise

$$w_2 = n_1 \frac{(v_2 \sqrt{a_1 - v_1 \sqrt{a_2}})^2}{v^2 v_2} + \left(p + \frac{a_2}{v_2 v_2^0} \right) \Delta v_2 \quad \left. \vphantom{\frac{(v_2 \sqrt{a_1 - v_1 \sqrt{a_2}})^2}{v^2 v_2}} \right\} \dots \dots (2)$$

¹⁾ In these differentiations many parts have not been taken into account. For in general v_1 and v_2 are still functions of n_1 and n_2 . But as the neglected parts in w_1 and w_2 can always be represented by $z_1 = \frac{\partial z}{\partial n_1}$ and $z_2 = \frac{\partial z}{\partial n_2}$, in which z , just as w , will always be a homogeneous function of the first degree with respect to n_1 and n_2 , necessarily $n_1 z_1 + n_2 z_2$ will have to be $= 0$, $n_1 w_1 + n_2 w_2$ already being $= w$ according to (2). Now also $n_1 z_1 + n_2 z_2 = z$, hence z is identically $= 0$, hence also z_1 and z_2 .

It would indeed not be difficult to show directly the disappearance of the parts z_1 and z_2 , which have been left out of account. As to z_1 , we get the result:

$$\frac{1}{v} \left(n_1 \frac{a_1}{v_1} + n_2 \frac{a_2}{v_2} \right) \left(n_1 \frac{\partial v_1}{\partial n_1} + n_2 \frac{\partial v_2}{\partial n_1} \right),$$

in which the last factor will disappear in consequence of $\frac{\partial v_2}{\partial n_1} = \frac{\partial v_1}{\partial n_2}$, as v_1 is a homogeneous function of the 0th degree with respect to the molecular numbers n_1 and n_2 .

For liquids p may of course always be cancelled against the so much greater molecular pressure a/v^2 .

We will just mention that the earlier — inaccurate — expressions were:

$$w_1 = n_2 \frac{(b_2 \sqrt{a_1} - b_1 \sqrt{a_2})^2}{b^2 b_1} \quad ; \quad w_2 = n_1 \frac{(b_1 \sqrt{a_1} - b_2 \sqrt{a_2})^2}{b^2 b_2}.$$

3. Volume contraction with normal components.

We must now try to find an expression for Δv , and then also for Δv_1 and Δv_2 , in order to be able to substitute in (1) and (2), and to form an opinion of the order of magnitude of the different parts. As

$$\Delta v = v - v_0 = v - (n_1 v_1^0 + n_2 v_2^0),$$

we have also:

$$\Delta v = b - (n_1 b_1 + n_2 b_2) + (v - b) - n_1 (v_1^0 - b_1) - n_2 (v_2^0 - b_2).$$

Now $b = n_1 b_1 + n_2 b_2$, hence after application of the equation of state, there remains:

$$\Delta v = \frac{(n_1 + n_2) RT}{p + a/v^2} - \frac{n_1 RT}{p + a_1/v_1^2} - \frac{n_2 RT}{p + a_2/v_2^2},$$

i.e. with neglect of p :

$$\Delta v = RT \left[(n_1 + n_2) \frac{v^3}{a} - n_1 \frac{v_1^0^2}{a_1} - n_2 \frac{v_2^0^2}{a_2} \right],$$

or

$$\begin{aligned} \Delta v = & \frac{RT}{a a_1 a_2} \left[(n_1 + n_2) (n_1 v_1^0 + n_2 v_2^0)^2 a_1 a_2 - n_1 v_1^0^2 a a_2 - n_2 v_2^0^2 a a_1 \right] + \\ & + \frac{RT}{a} (n_1 + n_2) \left(2 \Delta v (n_1 v_1^0 + n_2 v_2^0) + (\Delta v)^2 \right), \end{aligned}$$

as $v = (n_1 v_1^0 + n_2 v_2^0) + \Delta v$. In consequence of this, with $a = (n_1 \sqrt{a_1} + n_2 \sqrt{a_2})^2$:

$$\begin{aligned} \Delta v - \frac{(n_1 + n_2) RT}{a} \left(2 \Delta v (v - \Delta v) + (\Delta v)^2 \right) = \\ = \frac{RT}{a a_1 a_2} \left[(n_1 + n_2) (n_1 v_1^0 + n_2 v_2^0)^2 a_1 a_2 - (n_1 v_1^0^2 a_2 + n_2 v_2^0^2 a_1) (n_1 \sqrt{a_1} + n_2 \sqrt{a_2})^2 \right], \end{aligned}$$

which, worked out with neglect of Δv by the side of $2v$, and putting $n_1 + n_2 = 1$ at RT , gives:

$$\Delta v \left(1 - \frac{2 RT}{a/v} \right) =$$

$$\begin{aligned}
&= \frac{RT}{a_1 a_2} n_1 n_2 \left[\left\{ n_1 v_1^{\circ 2} + 2(n_1 + n_2) v_1^{\circ} v_2^{\circ} + n_2 v_2^{\circ 2} \right\} a_1 a_2 - \right. \\
&\quad \left. - \left\{ n_1 v_2^{\circ 2} a_1^2 + 2(n_1 v_1^{\circ 2} a_2 + n_2 v_2^{\circ 2} a_1) \sqrt{a_1 a_2} + n_2 v_1^{\circ 2} a_2^2 \right\} \right] \\
&= \frac{RT}{a_1 a_2} n_1 n_2 \left[n_1 \left\{ v_1^{\circ} a_2 \sqrt{a_1} \left((v_1^{\circ} + 2v_2^{\circ}) \sqrt{a_1} - 2v_1^{\circ} \sqrt{a_2} \right) - v_2^{\circ 2} a_1^2 \right\} + \right. \\
&\quad \left. + n_2 \left\{ v_2^{\circ} a_1 \sqrt{a_2} \left((v_2^{\circ} + 2v_1^{\circ}) \sqrt{a_2} - 2v_2^{\circ} \sqrt{a_1} \right) - v_1^{\circ 2} a_2^2 \right\} \right] \\
&= \frac{RT}{a_1 a_2} n_1 n_2 \left[n_1 \left\{ 2v_1^{\circ} a_2 \sqrt{a_1} (v_2^{\circ} \sqrt{a_1} - v_1^{\circ} \sqrt{a_2}) + a_1 (v_1^{\circ 2} a_2 - v_2^{\circ 2} a_1) \right\} + \right. \\
&\quad \left. + n_2 \left\{ 2v_2^{\circ} a_1 \sqrt{a_2} (v_1^{\circ} \sqrt{a_2} - v_2^{\circ} \sqrt{a_1}) + a_2 (v_2^{\circ 2} a_1 - v_1^{\circ 2} a_2) \right\} \right] \\
&= \frac{RT}{a_1 a_2} n_1 n_2 (v_1^{\circ} \sqrt{a_2} - v_2^{\circ} \sqrt{a_1}) \left[n_1 \left\{ (v_1^{\circ} \sqrt{a_2} + v_2^{\circ} \sqrt{a_1}) a_1 - 2v_1^{\circ} a_2 \sqrt{a_1} \right\} + \right. \\
&\quad \left. + n_2 \left\{ - (v_1^{\circ} \sqrt{a_2} + v_2^{\circ} \sqrt{a_1}) a_2 + 2v_2^{\circ} a_1 \sqrt{a_2} \right\} \right].
\end{aligned}$$

For the form between [] we may further write:

$$\begin{aligned}
&n_1 a_1 (v_1^{\circ} \sqrt{a_2} + v_2^{\circ} \sqrt{a_1}) - n_2 a_2 (v_1^{\circ} \sqrt{a_2} + v_2^{\circ} \sqrt{a_1}) - 2n_1 v_1^{\circ} a_2 \sqrt{a_1} + 2n_2 v_2^{\circ} a_1 \sqrt{a_2} \\
&= -n_1 a_1 (v_1^{\circ} \sqrt{a_2} - v_2^{\circ} \sqrt{a_1}) - n_2 a_2 (v_1^{\circ} \sqrt{a_2} - v_2^{\circ} \sqrt{a_1}) + \\
&\quad + 2a_1 \sqrt{a_2} (n_1 v_1^{\circ} + n_2 v_2^{\circ}) - 2a_2 \sqrt{a_1} (n_1 v_1^{\circ} + n_2 v_2^{\circ}),
\end{aligned}$$

so that we finally get:

$$\Delta v \left(1 - \frac{2RT}{a/v} \right) = \frac{RT}{a_1 a_2} n_1 n_2 (v_1^{\circ} \sqrt{a_2} - v_2^{\circ} \sqrt{a_1}) \left[\frac{2v_0 (\sqrt{a_1} - \sqrt{a_2}) \sqrt{a_1 a_2} - (n_1 a_1 + n_2 a_2) (v_1^{\circ} \sqrt{a_2} - v_2^{\circ} \sqrt{a_1})}{\left. \right\} \right]. \quad (3)$$

This almost quite exact result (only p has been neglected, and in the 1st member Δv by the side of $2v$) shows that Δv will be of the order $\sigma = v_1^{\circ} \sqrt{a_1} - v_2^{\circ} \sqrt{a_1}$, so that w consists of two parts, of which the first is of the order σ^2 (cf. equation (1)), the second of the order σ . When the critical pressures differ little, σ is very small, and of the small heat of mixing w the second part (neglected before) will certainly predominate.

In the case that the critical pressures differ little, expression (3) can be considerably simplified. For then $v_1^{\circ} \sqrt{a_2} - v_2^{\circ} \sqrt{a_1} = 0$ can be put between [], and there remains:

$$\Delta v \left(1 - \frac{2RT}{a/v}\right) = \frac{2RT}{a/v_0} n_1 n_2 \left(1 - \frac{v_2^0 \sqrt{a_1}}{v_1^0 \sqrt{a_2}}\right) \frac{v_1^0 \sqrt{a_2} (\sqrt{a_1} - \sqrt{a_2})}{\sqrt{a_1 a_2}}.$$

But because then $\sqrt{a_2} = \frac{v_2^0}{v_1^0} \sqrt{a_1}$, $\sqrt{a_1} - \sqrt{a_2} = \frac{v_1^0 - v_2^0}{v_1^0} \sqrt{a_1}$,

$$\text{hence } \Delta v \left(1 - \frac{2RT}{a/v}\right) = \frac{2RT}{a/v_0} n_1 n_2 \left(1 - \sqrt{\frac{p_{k_1}}{p_{k_2}}}\right) (v_1^0 - v_2^0). \quad (3a)$$

As for ordinary substances in liquid state (below the boiling-point) $a/v \sim 7RT_k$, and in the second member $v_0 = v$ may be put, we find with $T/T_k = m$:

$$\Delta v = \frac{2/7 m}{1 - 2/7 m} n_1 n_2 \left(1 - \sqrt{\frac{p_{k_1}}{p_{k_2}}}\right) (v_1^0 - v_2^0). \quad (3b)$$

If e.g. $m = 1/2$, we have with $n_1 = 1 - x$, $n_2 = x$ for Δv the value $1/6 x(1-x)(1-\sqrt{v_1^0 - v_2^0})$, so that the *maximum* contraction (at $x = 1/2$) becomes $= 1/24 (1-\sqrt{v_1^0 - v_2^0})$ — hence very small and of the order $1-\sqrt{v}$.

With regard to the *sign* of Δv it may be pointed out that $b_1 > b_2$, e.g. $b_1 = \theta b_2$ corresponds with $v_1^0 > v_2^0$. Then a_1 is approximately $= \theta^2 a_2$, so that a_1/b_1 becomes $= \theta^{a_2/b_2}$ or $T_{k_1} > T_{k_2}$. But from this it ensues that p_{k_1} is generally somewhat greater than p_{k_2} , in consequence of which $1-\sqrt{p_{k_1}/p_{k_2}}$ becomes negative. And the reverse when v_1^0 should be $< v_2^0$. The quantity Δv will, therefore, nearly always be *negative*, in other words volume contraction will take place.

With regard to the differential variations of volume $\Delta v_1 = v_1 - v_1^0 = \frac{\partial(\Delta v)}{\partial n_1}$ and $\Delta v_2 = v_2 - v_2^0 = \frac{\partial(\Delta v)}{\partial n_2}$, from the approximated expression (3a) follows, when a/v is considered constant in the correction term of the 1st member:

$$\Delta v_1 \left(1 - \frac{2RT}{a/v}\right) = 2RT n_2 (1-\sqrt{v_1^0 - v_2^0}) \frac{\partial}{\partial n_1} \left(\frac{n_1 v_0}{a}\right).$$

In approximation $v_1^0 \sqrt{a_2} = v_2^0 \sqrt{a_1}$ was taken, so that $\sqrt{a_1}$ is $= \frac{v_1^0}{v_2^0} \sqrt{a_2}$ and $\sqrt{a} = n_1 \sqrt{a_1} + n_2 \sqrt{a_2} = \sqrt{a_2} \left(n_1 \frac{v_1^0}{v_2^0} + n_2\right) = \frac{v_0}{v_2^0} \sqrt{a_2}$.

In consequence of this $\frac{\partial}{\partial n_1} \left(\frac{n_1 v_0}{a}\right)$ becomes $= \frac{\partial}{\partial n} \left(\frac{n_1 v^0 v_2^0}{a_2 v_0^2}\right) = \frac{v_2^0}{a_2} \frac{\partial}{\partial n_1} \left(\frac{n_1}{v_0}\right)$, in which $\frac{\partial}{\partial n_1} \left(\frac{n_1}{v_0}\right) = \frac{v_0 - n_1 v_1^0}{v_0^2} = \frac{n_2 v_2^0}{v_0^2}$. Hence we have

$\frac{\partial}{\partial n_1} \left(\frac{n_1 v_0}{a} \right) = n_2 \frac{v_2^0}{v_1^0} \frac{v_2^0}{a} = n_2 \frac{v_2^0}{a}$; therefore with the same approximation as (3a):

$$\text{and} \quad \left. \begin{aligned} \Delta v_1 \left(1 - \frac{2RT}{a/v} \right) &= \frac{2RT}{a/v_2^0} n_2^2 (1 - \sqrt{v_1^0 - v_2^0}) \\ \Delta v_2 \left(1 - \frac{2RT}{a/v} \right) &= \frac{2RT}{a/v_1^0} n_1^2 (1 - \sqrt{v_1^0 - v_2^0}) \end{aligned} \right\} \quad (4a)$$

We now duly get again $n_1 \Delta v_1 + n_2 \Delta v_2 = \Delta v_1$, because $n_1 n_2^2 \frac{v_2^0}{a} + n_2 n_1^2 \frac{v_1^0}{a} = n_1 n_2 \frac{v_0}{a}$.

4. Substitution of (3^b) in (1).

We get for w , after substitution of (3^a) in (1), with omission of the external pressure p :

$$w = n_1 n_2 \frac{(v_2^0 \sqrt{a_1 - v_1^0 \sqrt{a_2}})^2}{v_0 v_1^0 v_2^0} + \frac{a}{v v_0} \frac{^{2/7} m}{1 - ^{2/7} m} n_1 n_2 \frac{v_1^0 \sqrt{a_2} - v_2^0 \sqrt{a_1}}{v_1^0 \sqrt{a_2}} (v_1^0 - v_2^0),$$

or

$$w = n_1 n_2 \left[\frac{(v_2^0 \sqrt{a_1 - v_1^0 \sqrt{a_2}})^2}{v_0 v_1^0 v_2^0} - \frac{^{2/7} m}{1 - ^{2/7} m} \frac{(v_2^0 \sqrt{a_1 - v_1^0 \sqrt{a_2}})(v_1^0 - v_2^0) \sqrt{a}}{v v_1^0 v_2^0} \right],$$

when $v_2^0/v_0 \sqrt{a}$ is substituted for $\sqrt{a_2}$. With $m = 1/2$ and $v = v_0$, this passes into

$$w = \frac{n_1 n_2}{v_0 v_1^0 v_2^0} (v_2^0 \sqrt{a_1 - v_1^0 \sqrt{a_2}}) \left[(v_2^0 \sqrt{a_1 - v_1^0 \sqrt{a_2}}) - \frac{1}{6} (v_1^0 - v_2^0) \sqrt{a} \right] \quad (5b)$$

The factor $1/6$ is, of course, somewhat different, when $m = T/T_c$ is not $= 1/2$. When the critical pressures are equal, the foregoing factor is $= 0$, hence also the total heat of mixing. But when these pressures do not differ too much, the first term between [] will all the same be small with regard to the second, and in approximation

$$w = - \frac{1}{6} \frac{n_1 n_2}{v_0 v_1^0 v_2^0} (v_2^0 \sqrt{a_1 - v_1^0 \sqrt{a_2}}) (v_1^0 - v_2^0) \sqrt{a} \quad (5c)$$

may be written.

But however this be, we shall always be allowed to write:

$$w = n_1 n_2 \frac{\beta}{v_0 v_1^0 v_2^0} \quad ; \quad w_1 = n_2^2 \frac{\beta}{v_0^2 v_1^0} \quad ; \quad w_2 = n_1^2 \frac{\beta}{v_0^2 v_2^0},$$

or, as $v_0 = n_1 v_1^0 + n_2 v_2^0 = (1-x) v_1^0 + x v_2^0 = v_1^0 + x(v_2^0 - v_1^0) =$

$= v_1^0 (1 + rx)$, when $\frac{v_2^0 - v_1^0}{v_1^0} = r$ (hence $\frac{v_2^0}{v_1^0} = 1 + r$) is put, and with $\frac{\beta}{(v_1^0)^3} = \alpha$:

$$w = x(1-x) \frac{\alpha}{(1+rx)(1+r)}; w_1 = \frac{x^2 \alpha}{(1+rx)^2}; w_2 = \frac{(1-x)^2 \alpha}{(1+rx)^2(1+r)}, \quad (6)$$

the old expressions, but in which α has now a somewhat different value than before, and will also be dependent on the temperature (through m).

When in approximation

$$w = \frac{\alpha}{v v_0} \Delta v = \frac{\alpha}{v^3} \Delta v$$

is written for (1) with omission of the first part, which is generally much smaller, we get approximately:

$$\frac{w}{\Delta v} = \frac{\alpha}{v^3} \dots \dots \dots (7)$$

If the critical pressures of different substances do not diverge too much, also the values of α/v^3 do not lie far apart in mixtures of different pairs of substances, and we shall find values of at least the same order of magnitude for the quotient $\frac{w}{\Delta v}$; a result to which

also Mr. KATZ came experimentally in his latest paper (loc.cit.)¹⁾ — at least as far as volume-contraction and heat of imbibition of amorphous and crystalline swelling substances is concerned. That the ratios there are quite analogous to those of liquid mixtures is owing to this, that when one of the components is *solid*, it must first be reduced to the liquid state, whence the pure heat of melting of this components is simply added to w . But if Δv predominates, also *this* heat might be omitted with respect to the second part.

At any rate we shall never find exactly α/v^3 for $w/\Delta v$, because the omitted part can never be entirely disregarded. For this reason also the values of $w/\Delta v$ will differ somewhat, even with almost equal values of α/v^3 , which was also found by KATZ.

¹⁾ The curves of Fig. 1 and 2 are no hyperbolae, but *oblique parabolae*, as according to (6) w is $= \frac{x(1-x)}{1+rx} \frac{\alpha}{1+r}$. If r were $= 0$ ($v_2^0 = v_1^0$), the curve of the integral heat of mixing (i.e. $1-x$ gr. mol. of I + x gr. mol. of II) would be a pure parabola. If, however, v_2^0 is not $= v_1^0$, the top of the parabola will have been displaced somewhat to the side of the component with the smallest molecular volume, as is easy to verify. From $\partial w / \partial x = 0$ we find $x = 1 : (1 + \sqrt{1+r})$, which gives $x = 1/2$ for $r = 0$, but $x < 1/2$ for $r > 0$. ($v_2^0 > v_1^0$).

The values of α/v , in our above formulae always refer exclusively to the *liquid mixture*, even for *solid* components, for as we already remarked above: this solid component must first be thought liquid, so that after all we have always to do with *liquid* mixtures.

Now that through the formulae derived by us above, the *absolute* values of w and Δv are known, which Mr. KATZ so eagerly desired, the problem has become clearer. Also when the components should be associated, everything remains essentially the same, as I will shortly show in a concluding paper. But then the preponderating influence of Δv will still be more pronounced, in consequence of the great variation of volume on dissociation of the double molecules.

And finally as regards the "important as yet undiscovered principles of the laws that govern molecular attraction" — I believe that this principle too was solved long ago¹). This subject will also be discussed more fully in our concluding paper.

Tavel sur Clarens (Suisse), September 1922.

¹) Compare my papers in These Proc. Vol. XVIII N^o. 8, p. 1220—1235, and following numbers; in the Journ. de Ch. physique **14**, p. 1 et seq. (1916); in the Z. f. anorg. und allg. Chemie **104**, p. 57—156 (1918); in the Ch. Weekbl. of 1918 (p. 1124); in These Proc. Vol. XXI N^o. 5, p. 644—655, and the J. de Ch. ph. **16**, 411 (1919), which possibly have escaped Mr. KATZ's notice.

Histology. — *“On the Regeneration of Sensitive End-corpuscles after section of the nerve”*. By Prof. J. BOEKE.

(Communicated at the meeting of September 30, 1922).

During the process of regeneration of the motor endplates of striated muscles we are in a position to observe not only that the nerve-fibers put forth new shoots again and unite with the muscle-fibers to form new end-plates, but also that all the surrounding tissue elements: the connective tissue as well as the muscle-fibers, the nerve-sheaths and the axis-cylinders of the nerves themselves, play a part in the regeneration process and are instrumental in ensuring its success.

In the case of sensitive nerve-endings it is more difficult to observe this procedure: 1° because there is a greater variety in the shape of these endings than in that of the motor end-plates, 2° because many more varieties occur side by side in the same environment, and 3° because sensory endings generally offer greater difficulty in establishing the relation between the nerve-fibers and the surrounding cells than motor end-plates do.

Now in the cere of the duck's bill there are two sorts of sensory end-bodies, viz. those of GRANDRY and HERBST, which are very well adapted to such an investigation by their simple, well-defined structure.

We examined the regeneration after cutting the nerve. The operation was well sustained by the animals and in a short time the wound was healed in primam (among 24 cases one inconsiderable suppuration) without any injury to the animals.

After 4—5 days the severed nerves were completely degenerated; nothing was left of the axis-cylinder except a few granules staining brownish black by BIELSCHOWKY's method. After some days these also disappeared.

An alteration of GRANDRY's tactile cells or of HERBST's core-cells, described by GASIOROWSKI years ago after cutting the nerve, consisting in shrivelling of the cells and bulging and wrinkling of the nuclei, I have not been able to detect. In agreement with the aspect of the soles of the motor endings the protoplasm became more coarse-grained, swollen, while the impression was given that in the core

of HERBST's corpuscles there were more nuclei than the normal corpuscle presents. There also seemed to exist a slight increase in the number of the capsule-cells of GRANDRY's corpuscles.

While regenerating the nerve-fibers follow the old nerve-courses (which have changed into strands of BÜNGNER), and pass again into the primary corpuscles. It seems, however, that all along also new corpuscles, especially GRANDRY's corpuscles, are formed, in which process sheath-cells (lemnoblats) grow larger and become tactile cells, as HERINGA has established as to embryological development. As soon as the nerve-fibers have reached the tactile cells of GRANDRY, they branch out, grow sinuously round them, always embedded in the protoplasm of the capsule-cells and at length force their way between the tactile cells. Directly after this the neurofibrils begin to branch, broadening reticulations appear, which gradually spread between the tactile cells, first as a delicate retiform structure, afterwards as a close-mesh network. In this way the whole interspace between the two tactile cells is occupied again by a net-shaped neurofibrillar nerve-plate.

Two things strike us here as being remarkable:

First of all that in the beginning of the process of regeneration the nerve-fibers bend round the tactile cells in various convolutions and ramifications, but that in the following stages (after 2 or 3 months) this process is less pronounced, so that gradually the normal condition asserts itself in the same way as with the motor end-plates; secondly that neither the nerve-fibers themselves nor their terminal branches and terminal broadening ever run freely, but always remain enclosed in the protoplasm of the conducting cells and the capsule-cells, and that directly when they are within reach of the tactile cells, a peculiar network is formed around them, inside the protoplasm of the tactile cells, which could also be demonstrated, in complete distribution, in the normal corpuscles of GRANDRY; lastly that here the process of regeneration of the intraprotoplasmic network shows itself first round the end-branches (end-reticulations and end-knots) of the nerve-fibers and then appears to extend gradually over the whole extent of the flat tactile cells. The whole regeneration-process takes two or three months.

In the case of HERBST's corpuscles the in-growing nerve-fibers also follow the old nerve-tracks. At their point of entrance into the core of the corpuscle we see also here that the nerve-fiber not only proceeds linearly into the protoplasm of the syncytially connected cells of the core, but also that it throws out its branches and passes with many convolutions through the protoplasm, so that the aspect

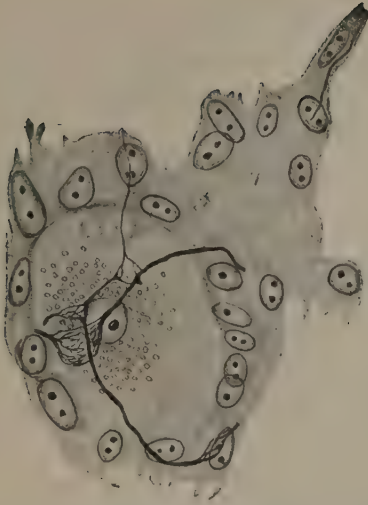


Fig. 1. GRANDRY's corpuscle. 36 days after cutting the nerve. Initial stage of the surface-enlargement in the neurofibrillar apparatus of the nerve-threads that grow round the tactile cells. Transverse section.



Fig. 2. GRANDRY's corpuscle, 46 days after cutting the nerve. Complete regeneration, double growth round the tactile cells. Longitudinal section.

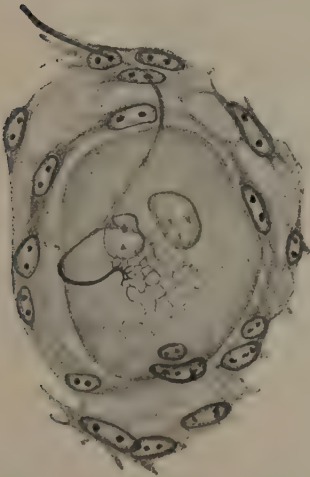


Fig. 3.

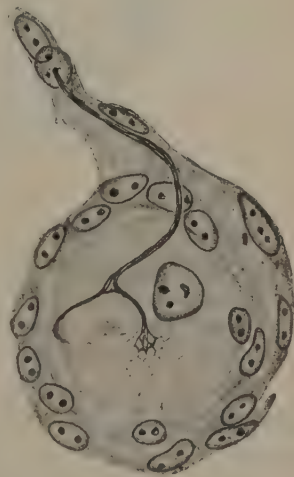


Fig. 4.

GRANDRY's corpuscle. 42 days after the cutting of the nerve. Transverse section of the same end-body at different planes. Splitting of the in-growing nerve-thread. Intrusion between the tactile cells, formation of a protoplasmic network (receptive substance, periterminal network) round the end-buds of the neurofibrillar nerve-apparatus.

of the whole structure becomes much more complicated than that of the primary nerve-fiber of the normal HERBST-corpuscles. However, here also the normal relations gradually assert themselves. I have not been able to ascertain whether new HERBST-corpuscles are forming in the course of the regeneration process.

Round the inner core in HERBST's corpuscles are disposed a large number of connective-tissue lamellae, separated by lymphspaces.

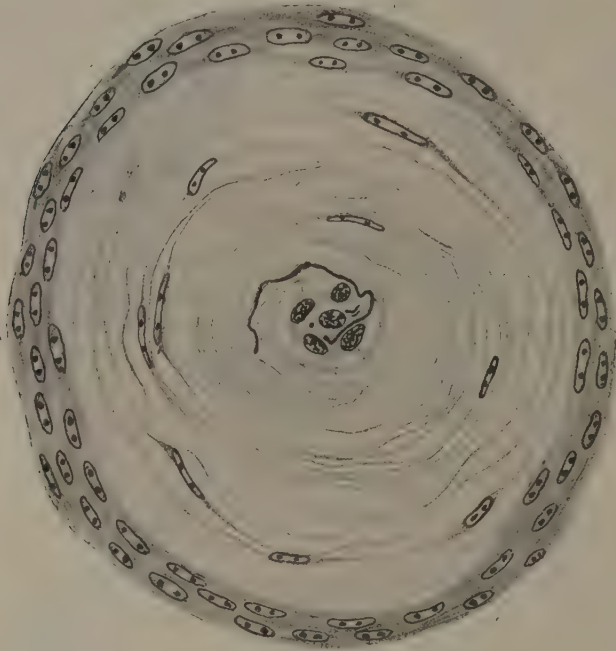


Fig. 5.

Transverse section of a HERBST-corpuscle, with a nerve-thread that not only branches out in the protoplasm of the cells of the core, but proceeds from there into the connective-tissue lamellae round the inner core, where it continues its growth. 42 days after the cutting of the nerve.

These lamellae are connected by means of cellular processes, thus forming a whole.

Now in watching the regeneration it may be repeatedly observed that the nerve-thread, which has passed into the inner core of a HERBST-corpuscle and ramifies in the protoplasm of the core, does not remain enclosed here in its entirety, but that some of the end-branches leave the core and intrude into the tissue of the connective-tissue lamellae. This then is the very place to see quite clearly,

that these nerve-fibers do not force their way into the lacunae between the connective-tissue lamellae, but that they lie in the lamellae, enveloped by protoplasm, and remain there. This envelop must decidedly partake of the nature of connective tissue. This observation, therefore, is in perfect harmony with what could previously be established for the neuromuscular spindle of striated muscles. In them also the in-growing regenerating nerve-threads could be seen moving through the protoplasm of the connective-tissue cells of the capsular space, which cells have developed into a conductive-tissue.

Utrecht, August 1922.

Chemistry. — "*Heterogeneous catalysis and the orientation of adsorbed molecules*". By Prof. H. R. KRUYT and C. F. VAN DUIN.

(Communicated at the meeting of September 30, 1922).

In a previous communication¹⁾ we published investigations on the relation between the adsorption of reacting substances and the velocity of the reaction, with the object of coming to a better understanding of heterogeneous catalysis. In these investigations we found, that by giving coal to the reacting system a decrease of the velocity sets in, even in cases, where undoubtedly an increase of the reacting components in the surface layer takes place.

In accordance with the theory of I. LANGMUIR²⁾ and W. D. HARKINS²⁾ concerning the special condition of molecules, which are situated in surface layers, we tried to explain our results by the assumption 1. that adsorbed molecules have partly lost their mobility and consequently a great deal of the possibility of meeting and reacting with other molecules, and 2. that adsorption can cause positive catalysis only in the case, when the molecules are adsorbed in such a way that the number of effective collisions increases.

That adsorption in itself can have a decreasing effect was found when studying a monomolecular reaction, viz. the transformation of racemic dibromo-succinic acid into bromo fumaric acid and HBr³⁾. The results are given in the tables I and II.

Evidently a marked decrease in the velocity occurs.

We discussed in the paper cited above, that a positive contact catalysis can be expected only in the case, when the reacting group is turned away from the adsorbent and towards the surrounding liquid. With charcoal as an adsorbent, and water as milieu, all electrically polar groups will be turned towards the water; we therefore had chosen the reaction of $\alpha\beta$ dibromo-propionic acid and KJ (formation of acrylic acid, KBr and J₂). As might have been

¹⁾ Rec. trav. chim. Pays Bas **40**, 249 (1921).

²⁾ Journ. amer. chem. Soc. **39**, 354 en 541 (1917).

³⁾ Journ. amer. chem. Soc. **38**, 2221 (1916) and **39**, 1848 (1917).

⁴⁾ Cf. HOLMBERG, Journ. f. prakt. Chem. **84**, 145 (1911) and Zeitschr. f. physik. Chem. **79**, 147 (1912).

TABLE I. *Without coal.*

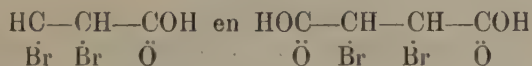
Time in min.	c.c. NaOH $\frac{1}{20}n$ p. 10 cc.	conc. in $\frac{n}{400}$	k mono- mol.
0	20.22	19.98	—
1371	21.53	17.36	0.000103
2991	22.70	15.02	095
4288	23.57	13.28	095
6771	24.88	10.66	.093

TABLE II. *With coal.*

Time in min.	c.c. NaOH $\frac{1}{20}n$ p. 10 cc. not corr.	c.c. NaOH $\frac{1}{20}n$ p. 10 cc. corr.	conc. in $\frac{n}{400}$	k mono- mol.
0	18.91	20.22	19.98	—
1372	19.89	21.20	18.02	0.000075
2992	20.87	22.18	16.06	73
4311	21.29	22.60	15.22	63
6788	22.12	23.43	13.56	57

expected, we then have found an acceleration of the reaction. We repeated these experiments in a CO_2 -atmosphere and in the dark room to avoid complications. The result was almost the same: without coal we found $k = 0.000123$ and when coal was added $k = 0.000149$.

The place of the polar groups in dibromo-propionic acid is however not symmetric; the possibility remains that the COOH -group exerts a more vigorous orientating influence than the Br groups and consequently the latter will not be in a most favourable condition. A better result could be expected therefore in the case of the reaction of dibromo-succinic acid and KJ . A comparison between the formulae



will elucidate this immediately. Moreover, the stereochemical configuration suggests a still better arrangement in the case of the mesoform than in that of the racemic. In the tables III and IV we give the results obtained with the racemic, in the tables V and VI

TABLE III.
Racemic-acid without coal.

Time in min.	c.c. thio $\frac{n}{40}$	conc. $n/800$	k mono- mol.
0	0.08	19.92	—
790	1.82	18.18	0.000116
1392	2.99	17.01	113

 k mean 0.000115TABLE IV.
Racemic-acid with coal.

Time in min.	c.c. J $\frac{n}{40}$ not corr.	c.c. J $\frac{n}{40}$ corr.	conc. $n/800$	k mono- mol.
0	17.27	20.12	19.92	—
776	11.72	14.57	14.37	0.000421
1380	8.90	11.75	11.55	395

 k mean 0.000408

TABLE V.
Meso-acid *without* coal.

Time in min.	c.c. thio $\frac{n}{40}$	conc. $\frac{n}{800}$	k mono- mol.
0	0.06	19.94	—
289	1.11	18.89	0.000187
576	2.12	17.88	189
806	2.83	17.17	186

k mean 0.000187

TABLE VI.
Meso-acid *with* coal.

Time in min.	c.c. J $\frac{n}{40}$ not corr.	c.c. J $\frac{n}{40}$ corr.	conc. $\frac{n}{800}$	k mono- mol.
0	18.21	20.14	19.94	—
292	14.45	16.38	16.18	0.000716
582	11.20	13.13	12.93	744
809	9.47	11.40	11.20	713

k mean 0.000724

those with the meso-acid. The initial concentration of the acid was $\frac{1}{40}$ n., that of KJ 2n.; work is done at 25° centigrade, in CO₂-atmosphere, in the dark room; 1 gramm of coal was added per 100 ccm.; in the experiments with $\frac{1}{2}$ coal 10 ccm. of the reacting mixture were poured into 20 ccm. of thio-solution of 0.02525 n.; the titration was done with a J-solution of $\frac{1}{40}$ n.

These results, shewing a great acceleration of the reactions, fully support our theory.

We have still other experience, which is in accordance with this theory. Dr. C. F. VAN DUIN wil give presently a detailed paper in *Recueil des Travaux chimiques des Pays Bas*.

Utrecht, VAN 'T HOFF-laboratory,
St. Andrews, United College of St. Leonards
and St. Salvador 1922.

Geology. — *“Fractures and Faults near the Surface of Moving Geanticlines. II. Abnormal Strikes near the Bending-points of the horizontal projection of the Geanticlinal axis.”* By Prof. H. A. BROUWER.

(Communicated at the meeting of September 30, 1922).

In a previous paper¹⁾ we have pointed to the occurrence of considerable transverse fractures near the bending points of the horizontal projection of the geanticlinal axis, which phenomenon has been explained by velocity differences on either side of these bending points.

Another phenomenon that may be observed near the bending points is the occurrence of older strikes, inclined or normal to the horizontal projection of the axis²⁾. This may be seen in rows of islands if the strikes in some islands do not coincide with the main trend of the islands. It is of great interest for determining the precise movements of the rows of islands, as will be shown in the following discussion.

The row of Islands Sermata-Islands, Babber, Tenimber-Islands.

In the islands Letti, Moa, Luang and Sermata the principal strikes are sometimes more or less parallel to the direction of the row, e.g. in Letti.

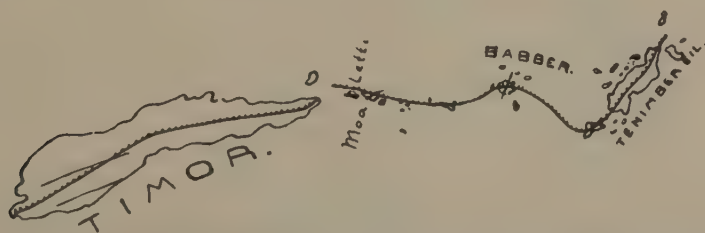


Fig. 1.

----- Horizontal projection of the geanticlinal axis (schematic representation).
 ——— Older strikes and coastlines.

In Moa some strikes are N.N.E. to N.E., so these are different from the direction of the row; in Luang the permian strata are

¹⁾ These Proceedings XXIII, p. 570,

²⁾ H. A. BROUWER, The horizontal movement of geanticlines and the fractures near their surface. Journ. of Geology. XXIX, 1921, p. 560–577.

intensely folded, with strong differences in strike and dip. If we construct the geanticlinal axis, as is generally done, with right angled bends, near Babber and near the southmost island Selaru of the Tenimber-Islands, so that the geanticlinal axis between these two islands is below the surface of the sea, the Tertiary strike in Babber (N.N.E.) is *about normal to the direction of the row*.

The connection of Halmaheira with the Pelew Islands.

The soundings between these islands do not go against the assumption that the prolongation of the Northern Peninsula of Halmaheira via Morotai towards the Helena-reef has a more or less east-western direction and bends in a more or less north-eastern direction towards the Pelew Islands. Even if considerable depths



Fig. 2.

..... Horizontal projection of the geanticlinal axis (partly hypothetic).
 — Older strikes and coast-lines.

should exist where the E-W. prolongation of Halmaheira's northern peninsula is supposed to be, these depths may be the result of gaping fractures, that may exist near the bending-point. The known strikes on Morotai are in the direction of the longer axis of the island and are oblique to the supposed direction of the geanticlinal axis. This conception renders the resemblance between the outlines of Celebes

and Halmaheira more complete. The difference between them consists chiefly in the eastern part of the northern peninsula of Halmaheira being covered by the sea.

The row Formosa—Riukiu-Islands.

The prolongation of the Sakishima-group is generally considered to be linked to North-Formosa¹⁾, also by authors whose interpretation of the known facts differs from the one that will be put forward

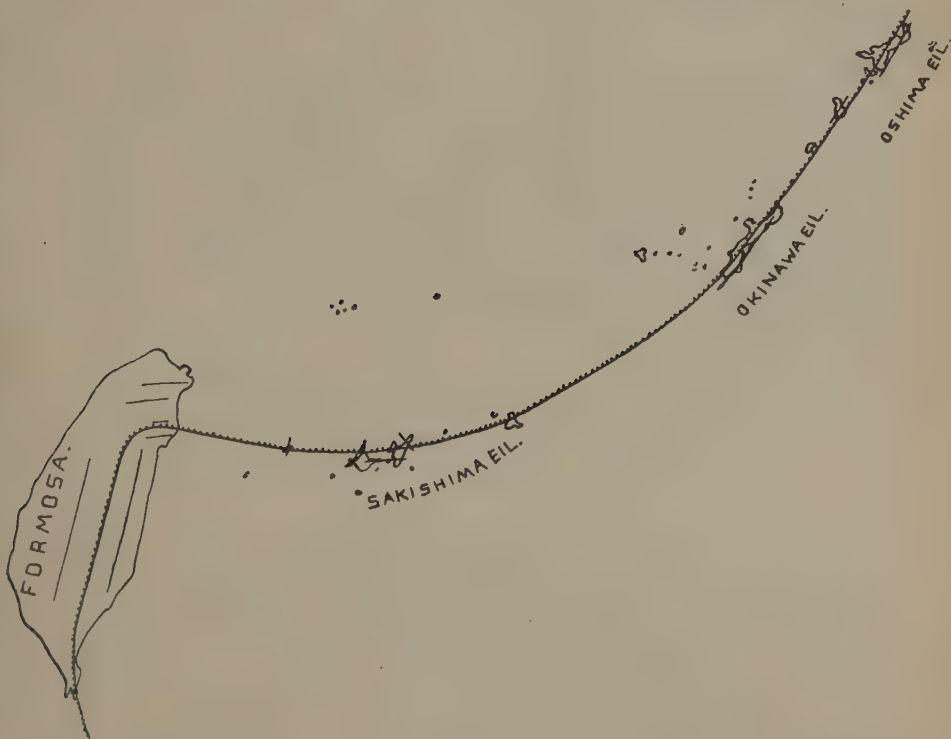


Fig. 3.

Explanation of Fig. 2.

lower down. The older strikes in the major part of Formosa are N.N.E. approximately parallel to the longer axis of the island. In North Formosa, however, their trend is about E—W, and they are cut off by the eastern coastline. In the Sakishima-group of the Riukiu-islands the strikes are irregular and are oblique or normal to the trend of the row of islands, while in the major part of the Riukiu

¹⁾ S. YOSHIWARA, Geologic structure of the Riukiu Curve etc. Journ. Coll. of Science, Tokyo. XVI. Part I, 1901.

Islands as far as Kiusiu the strikes are again about parallel to the direction of the row. This example seems to be similar to the two preceding ones, but the areas near Babber, as well as those near Morotai, from which this analogy might appear, are covered by the sea. In Formosa the bending of the older strikes is visible and moreover it can be seen that locally *near the bending point of the horizontal projection of the geanticlinal axis the older strikes are normal, or approximately so, to this projection, while on either side they are parallel to it.*

The movement at the surface of horizontally moving geanticlines.

In another publication we have already pointed to the difference in speed and direction of the movements at different depths¹⁾. The points, which were originally on the same vertical line, will in a later stage form an irregular curve in space. If the rate of movement has a vertical component, the vertical movement near the surface will be influenced by the vertical movement at greater depth.

The complicated horizontal and vertical movements, which differ already at a comparatively short distance, will cause new portions of the surface to form the crests of the moving geanticline. The direction of the older strikes with regard to the new geanticlinal axis in a subsequent phase of the movement, will depend upon the rate of movement at greater depth and that near the surface and upon the rate of erosion.

If the forces, which cause the movement of a geanticline, of which the highest parts rise above the sea-level as rows of islands, are deep-seated, the vertical movements will cause the uplift or subsidence of the islands, while the rate of horizontal movement at greater depth may differ considerably from the rate near the surface. We distinguish two extreme types of movement: 1° The horizontal movement near the surface is equal to zero. 2° The horizontal movement near the surface is similar to the movement at greater depth. In general neither of the extreme types will occur. In the first case no horizontal fracture-movements will take place at the surface, and straits generally correspond with a depression, islands with a culmination of the geanticlinal axis in a given stage of the movement.

In the second case the islands as such move^o in a horizontal direc-

¹⁾ H. A. BROUWER, The horizontal movement etc. loc. cit.

Id. The major tectonic features of the Dutch East Indies. Journ. Wash. Acad. of Sciences, 1922, p. 172—185.

tion, and straits may originate near the fractures without a subsidence of the geanticline along the axis. The movements near the surface are not equal to those at greater depth. But we suppose an extreme case, in which, considering broadly, the portions near the surface move at the same rate as those at greater depth.

The vertical movement and the effect of erosion.

Considering that during the movement erosion will continuously be at work in the portions above the sealevel, it will generally be possible to compare in the terminal phase the direction of the geanticlinal axis with the direction of the exposed older strikes. In case of a brief and not very intensive erosion, the tectonic details of a more plastic deformation at greater depths, are still invisible. The intensity of erosion decreases if, as in many rows of islands, the deformation of the geanticline takes place near the surface of the sea, and it is especially, when the vertical component of the rate of movement is great, that the tectonic details, which have been formed by a more plastic deformation at greater depth will soon be visible.

Rectilinear old strikes and curved geanticlinal axis with a bending-point in the last phase of movement under consideration.

The two extreme cases, mentioned above are :

1. *No horizontal movement at the surface.*

In the case represented by fig. 4 the old strikes cut the geanticlinal axes of the terminal phase on either side of the bending-point of $A'B'$ at an angle of about 45° , while nearer to A' and B' the older strike will gradually coincide with the new geanticlinal axis. If we assume that in the portions AC and DB , the movement has

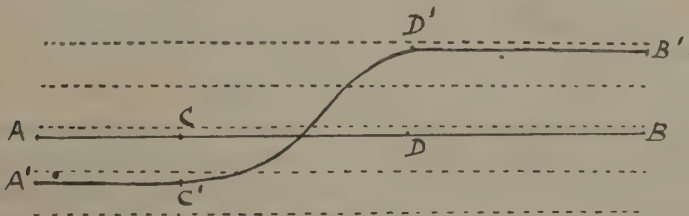


Fig. 4.

----- Older strike.

$A C B$ = horizontal projection of the geanticlinal axis in the initial stage of the movement under consideration.

$A' C' D' B'$ = Ibid. in the last phase of the movement under consideration.

taken place without velocity-differences and normal to the geanticlinal axis, gaping fractures will nevertheless be lacking in the portion $C'D'$, and in the case of a row of islands a strait will correspond with a minimum of the vertical projection of the geanticlinal axis.

2. *Horizontal movement at the surface, corresponding with the movement at greater depth.* In the portion $C'D'$ gaping fractures will be formed which — in so far as they occur near the surface of the sea — may be visible as straits between the islands.

In the positions $A'C'$ and $B'D'$ the old strikes will not differ from the direction of the new geanticlinal axis; to what extent they will do so in the portion $C'D'$, will depend on the movements near the surface. If these movements are non-rotational, differences up to 45° will occur; with rotation of the portions of the fractured surface the differences may be approximately zero.

Curving older strikes with a bending-point, and curving geanticlinal axis with displaced bending-point in the final stage.

One of the numerous variations of this more general case is represented in Fig. 5.

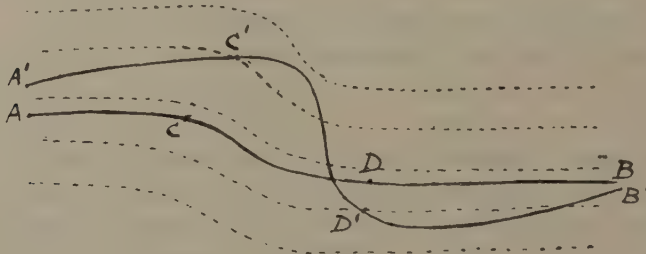


Fig. 5.

----- = Older strike.

$A C D B$ and $A' C' D' B'$ = horizontal projection of the geanticlinal axis, resp. in the initial-, and the terminal stage of the period under consideration.

1. *No horizontal movement at the surface.* In the final stage the old strikes are nearly all oblique to the geanticlinal axis, near the bending-point even approximately normal to it. Straits will correspond with depressions of the geanticlinal axis. If the geological structure changes chiefly in the direction vertical to the old strike, islands of highly different structure will in some places be located side by side.

2. *Horizontal movement at the surface corresponding with that at greater depth.* When, in the terminal stage of the considered period of movement, the points A , B , C and D have reached respectively

A' , B' , C' and D' , gaping fractures will appear all along the line $A' C' D' B'$, which may have helped to form straits. If during their displacement the parts near the surface had at the same time rotating movements, the angles between the old strikes and the geanticlinal axis may approach zero in the final stage.

Explanation of the abnormal strikes near the bending-points.

The abnormal strike of the island of Babber (fig. 1) may be accounted for by assuming that the deformation of the geanticline at greater depth has been attended with similar horizontal movements near the surface, so that e.g. the geanticlinal portion near the surface of the Tenimber Islands may originally have been situated N.N.E. of Babber, while these parts have since been displaced considerably relative to each other in a horizontal direction.

When assuming that no horizontal movement has taken place near the surface, the abnormal strike in Babber may also have originated from the great velocity-differences in a horizontal direction at greater depth, with this difference that the submarine geanticlinal part between Babber and the Tenimber-Islands is not disrupted near the surface. If the bending-point is the horizontal projection of a point that gives a minimum in the vertical projection, it may be that near it a large part of the geanticlinal axis is below the sea. In that case data will be lacking for a comparison of the present morphology with the older tectonic structure of the parts on either side of the bending-point.

Likewise the connection of Halmaheira with the Pelew-Islands is covered by the sea in a considerably area on either side of the bending-point, but in Morotai, where the older strike is oblique to the geanticlinal axis, the geanticline still emerges from the sea, while here the resemblance of the coastline to that of the neighbouring part of Halmaheira points to horizontal movements of the islands as such. In the row Formosa-Riukiu Islands (Fig. 3), unlike in the preceding instances, the bend of the older strikes is not covered by the sea, which facilitates a more correct explanation of the phenomenon. The dips in the older formations of the Taiwan-mountains in Formosa point to WNW. movements, those in North-Formosa to southward movements, those in the major part of the Riukiu-Islands to S—E movements. It is evident therefore, that already during the older phases of the orogenetic process, there was a tendency to form a bending-point between Formosa and the Riukiu-Islands. Similar movements during the youngest phase of the mountain-building process gave origin to numerous fractures, e.g. those which

cut off the E- W strikes of North-Formosa at a right angle and separate the Sakishima Islands from each other and from Formosa.

According to our conception of the differences in character and rate of movement at different depths, the absence of islands between Formosa and the Sakishima Islands may be looked upon as resulting from the formation of gaping fractures, in connection with the velocity-differences in a horizontal direction at the surface near the bending-point, and from a minimum elevation of the geanticline near the bending-point of the horizontal projection of the axis. The abnormal strikes of the Sakishima-Islands find an explanation in the assumption of movements, such as have been referred to above in the discussion of a geanticlinal movement with curving older strikes and with a displaced bending-point in the final stage (Fig. 5). The movement can be described only in broad outlines, the details cannot be derived from the visible facts. Thus the strikes on the Sakishima-Islands have no constant direction, and differences occur between the strikes of the older and those of the more recent deposits. Near the bending-point, however, irregular movements can be expected, while at the same time the rate of vertical movement, and consequently the rate of erosion must in a high degree have influenced the present-day tectonic structure.

The abnormal strikes of the Sakishima-Islands have been explained differently by VON RICHTHOFEN¹⁾, who speaks of transverse subsidence causing an abnormal dip of the strata in connection with his explanation of the origin of the mountain arcs of Eastern Asia by tensional and not by compressional stress. In contradistinction to this interpretation by *vertical* movements, we have compared the features with those of other belts of islands and find an explanation of the abnormal strikes near the bending-points of the geanticlinal axis in considerable *horizontal* movements, which have already been discussed by us for various geanticlines in connection with other features.

¹⁾ F. VON RICHTHOFEN, Geomorphologische Studien aus Ost-Asien. III. Sitz. Ber. Akad. d. Wiss. Berlin. Phys.-math. klasse. 1902, p. 944 et seq.

Chemistry. — "*Cyclic Derivatives of Mannitol*". By Prof. P. VAN ROMBURGH and J. H. N. VAN DER BURG.

(Communicated at the meeting of October 28, 1922).

Many years ago the researches on the decomposition of the formates of polyhydric alcohols, and also those on the 1.3.5. hexatriene, induced one of us (v. R.) in collaboration with Mr. VAN MAANEN, to study the action of formic acid on mannitol.¹⁾

After they had succeeded in preparing the hexaformate of mannitol it appeared against expectation that on being heated this substance yielded no hexatriene or only traces of it; on the other hand it yielded a product of the formula C_6H_8O , though in small quantities. This product, which boiled at $107-109^\circ$, had already been obtained by FAUCONNIER²⁾, together with isomannide, on heating mannitol with formic acid.

Also the tetraformate of mannitane and the diformate of isomannide were obtained by heating mannitol and formic acid, both in pure state. FAUCONNIER³⁾ found already, that by heating the diformate of isomannide only carbon oxide was evolved, with formation of isomannide; when on the other hand the former was heated, carbonic acid gas was formed, and again the oxide C_6H_8O was obtained.

The following constants were found for this latter product, which is very strongly levo-rotatory. Bp. 107° , $d_{15}^{15} = 0,9226$, $n_{D_{16}} = 1,3567$. With bromine it gives a liquid dibromide, $C_6H_8Br_2O$, $d_{15}^{17,5} = 0,8622$, Bp. 15 mm. $118^\circ.5$. A tetrabromide could not be obtained.

Reduction with hydrogen, according to SABATIER and SENDERENS, gave with C_6H_8O , both at 110° and at 180° a product of the formula $C_6H_{10}O$, which did not boil constantly under ordinary pressure but at 16° at 23 mm. Hence only 1 mol. of hydrogen had been absorbed.

In virtue of the decomposition of the di-formate of isomannide, in which only carbon oxide is formed, (so that it may be assumed not to

¹⁾ VAN MAANEN, Diss. Utrecht, 1909.

²⁾ C. r. 100, 914 (1885).

³⁾ Bull. Soc. Chim. N.S. 41, 125 (1884).

contain two vicinal OH-groups) VAN ROMBURGH and VAN MAANEN

proposed among others the formula $\text{CH}_2 \cdot \overset{\text{OH}}{\underset{\text{O}}{\text{CH}}} \cdot \text{CH} \cdot \text{CH} \cdot \text{CH} \cdot \text{CH}_2$, for

isomannide, and $\text{CH}_2 \cdot \overset{\text{O}}{\text{CH}} \cdot \text{CH} \cdot \overset{\text{OH}}{\underset{\text{OH}}{\text{CH}}} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{OH}$

for mannitane, the formate of which gave only carbon dioxide.

The compound $\text{C}_6\text{H}_8\text{O}$ might therefore be represented by the formula $\text{CH}_2 \cdot \text{CH} : \text{CH} \cdot \text{CH} \cdot \text{CH} : \text{CH}_2$, hence it would be α -vinylidihydrofurane.

In 1917 WINDAUS and TOMICH¹⁾ too studied the compound $\text{C}_6\text{H}_8\text{O}$, and could obtain by its reduction with hydrogen under the influence of palladium, an addition of two mol. of hydrogen, so that $\text{C}_6\text{H}_{12}\text{O}$ was formed, which substance according to them should be identical with a δ -hexylene oxide described by LIPP²⁾, in which not a 5-ring, but a 6-ring occurs: $\text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH} - \text{CH}_2$, so that the

original oxide would have the formula $\text{CH} : \text{CH} \cdot \text{CH} : \text{CH} \cdot \text{CH} \cdot \text{CH}_2$.

They concluded to the identity of the two saturated oxides by the equality of the boiling-point, both of the oxides and of the dibromides derived from them. WINDAUS rejects the possibility of the oxide being a furane-derivative, because then no asymmetric formula would be possible. This argument is, however, not valid with regard to the formula drawn up above.

It has appeared from investigations on the action of ozone on the oxide $\text{C}_6\text{H}_8\text{O}$, undertaken by Mr. BRUINS in the Utrecht Laboratory after the publishing of WINDAUS and TOMICH's paper, that in this reaction only carbonic acid, formaldehyde, and formic acid could be found, but no products in which a CH_3 -group occurs, which pleads against WINDAUS's formula. This, however, did not give a rigorous proof for the α -vinylidihydrofurane-formula. To obtain perfect certainty, we have followed another course.

First of all by reduction of $\text{C}_6\text{H}_8\text{O}$ with hydrogen of a pressure of two atmospheres in the presence of palladiumsol the saturated

¹⁾ Göttinger Nachrichten Math. Phys. Kl. 1917, S. 462.

²⁾ B. 18, 3275 (1885).

oxide $C_6H_{11}O$ was prepared. We used for this purpose an apparatus as indicated by SKITA¹⁾, in which the process of the reaction can be easily followed. During the fractionation the substance polymerizes partially, so that a perfectly pure product only can be obtained at the expense of considerable loss.

In spite of careful purification the possibility exists therefore that a small quantity of unsaturated product is left behind.

The substance was optically inactive, and showed the following constants:

$$\text{bp. } 103^\circ\text{—}106^\circ, d_{16}^{16} 0.8693, n_D 1.42797$$

(analysis: found C 71.8 H 12.3; calc. C 72.0 H 12.0).

In the way indicated by LIPP loc. cit. we have further prepared the δ -hexylene oxide, with the following constants:

$$\text{bp}_{767} 106^\circ\text{—}106^\circ.2, d_{16}^{16} 0.8617, n_D 1.41887.$$

Since on reduction α -vinylidihydrofurane must yield γ -hexylene oxide, we have also prepared this oxide according to WOHLGEMUTH²⁾, who however, only gives its boiling-point, viz. $106^\circ\text{—}108^\circ$ at 770 mm.

The following constants were found: $\text{Bp}_{760} 106^\circ.5\text{—}107^\circ, d_{16}^{16} 0.8609, n_D 1.41685$.

The corresponding bromides were obtained by treatment of these oxides with the 8-10-fold volume of hydrobromic acid (48 %) in a sealed tube for 1 to 2 hours at 100° . The 1-5-dibromo hexane boiled at 15 mm. at $105^\circ\text{—}108^\circ$ (analysis found Br. 65.3 % calc. 65.5), the 1-4-dibromo hexane at $106^\circ\text{—}108^\circ$ at 15 mm. (Br. found 65.4). The boiling-point of the di-bromide obtained from the reduced oxide $C_6H_{11}O$ was $106^\circ\text{—}110^\circ$ at 14 mm. (Br. found 65.6). It is evident that from the equation of the physical constants, both of the oxides and of their di-bromides, no conclusion can be drawn about the structure of the reduced oxide $C_6H_{11}O$, unless there are large quantities of the substances at our disposal. It was, therefore, necessary to try to obtain crystallized compounds. An attempt to prepare crystallized benzoates of the glycols corresponding with the dibromides did not meet with success. The action of piperidine on the di-bromides, on the other hand, in which quaternary ammonium bromides were formed, had a favourable result.

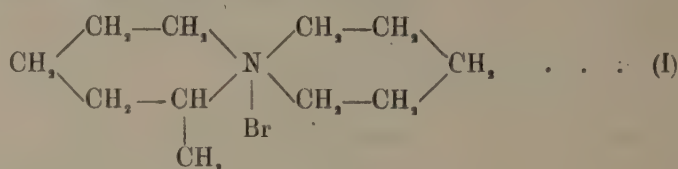
In analogy with VON BRAUN³⁾, who made act 1-5-dibromo pentane

¹⁾ B. **45**, 3595 (1912).

²⁾ C.r. **159**, 80 (1914).

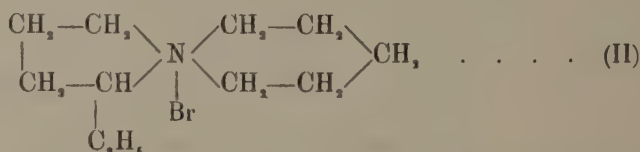
³⁾ B. **39**, 4347 (1906).

on piperidine in excess, we prepared, from the 1-5-dibromide, the α -methylpentamethylene piperidinium bromide:



By recrystallisation from alcohol-ether it is obtained as a white crystalline substance, melting above 290° (Br found 32.63, calc. 32.5).

In an analogous way the 1-4-dibromide yielded the α -ethyltetramethylene piperidinium bromide:



This substance melted at 270° corr. (Br 32.58 found, 32.5 calc.).

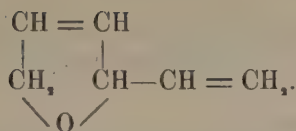
The dibromide obtained from the reduced oxide, $\text{C}_6\text{H}_{11}\text{O}$, treated in the same way, yielded a substance melting at 269° (corr.). (III). A mixture of this substance and the preceding one melted sharply at 269° corr.

Hence the 1-4-hexane dibromide and the dibromo derivative of the reduced oxide are identical.

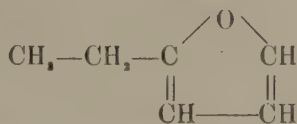
Moreover we prepared double salts with platinum chloride which likewise present the same analogy in their melting-points and in those of their mixtures.

From (I)	$(\text{C}_{11}\text{H}_{22}\text{NBr})_2$	PtCl_4	Pt. found 23.4	} calc. 23.5
	M.P. 247°	corr.		
From II	M.P. 260°	" "	" " 23.5	
From III	M.P. 259°	" "	" " 23.4	
Mixed melting-point I and II				246° corr.
" "	" "	II and III	260°	" "

Here again appears the analogy between the compound obtained from the 1-4-oxide and that which was prepared from the reduced oxide, $\text{C}_6\text{H}_{11}\text{O}$. Consequently this reduced oxide may really be regarded as α -ethyltetrahydrofuran and the unsaturated oxide $\text{C}_6\text{H}_8\text{O}$ of FAUCONNIER as α -vinylidihydrofuran:



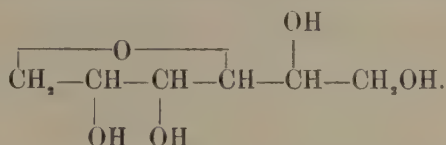
The place of the double bonds in this compound is now exactly known. The substance being optically active, an asymmetric carbon atom must be present in it; a formula, e.g. as the following:



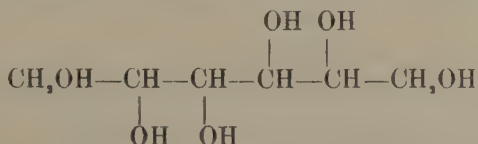
would not satisfy, as has also been remarked by WINDAUS.

As α -vinylidihydrofuran is formed from mannitane tetra formate, it is now possible to draw up a structure formula for the anhydrides of mannitol, viz. mannitane and isomannide.

We then arrive at the following scheme for mannitane:



In connection with the spatial formula of mannitol:

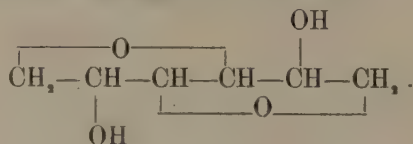


We see that as soon as the oxide-ring is formed between the C-atoms 1 and 4, the OH-groups at 2 and 3 will be at the same side. Besides the molecule contains two OH-groups situated beside each other at 5 and 6 (in perfect accordance with the pyrogenic decomposition of the tetra-formate, in which formic acid and carbon dioxide are split off from OH-groups placed beside each other), so that here a possibility must be for the formation of a di-acetone compound. In fact this compound was obtained as a colourless substance crystallizing in glossy leaflets, melting-point 155° (analysis C 58.83, H 8.38; calculated C 59.0 H 8.2).

The conductivity of boric acid will also be increased greatly by mannitane. ¹⁾

¹⁾ BÖSEKEN, Rec. 40, 553 (1921).

Through the formation of a second oxide ring, we then arrive at the following formula for the second anhydride



The places of the OH-groups here are at 2.5; hence no acetone derivative can be formed, nor will the conductivity of boric acid be raised. On treatment with acetone and 1 % hydrochloric acid the isomannide was actually recovered. The results of the measurements of the conductivity are recorded in the following table:

Capacity of the vessel 0.4106. Conductivity of the boric acid 0.5 mol. Litre $30 \times 10^{-6} = K_3$.							
	In water			In boric acid sol.			$K_1 - (K_2 + K_3)$.
	A.	W.	$K_2 \times 10^{-6}$	A.	W.	$K_1 \times 10^{-6}$	
Mannitol	500	5660	72.5	500	1037	396	294
Mannitane	500	3240	126.8	500	440	933	776
Isomannide				480	11000	34.4	4.4

The concentrations were 0,2 mol./Litre.

After deduction of the conductivity for water 3×10^{-6} , we find therefore that iso-mannide in a very small, quite negligible degree increases the conductivity, whereas this increase for mannitane exceeds that of mannitol more than $2\frac{1}{2}$ times.

Of the forgoing we may conclude that the structure of the unsaturated oxide C_6H_8O is proved, likewise that of mannitane. The given formula for isomannide seems to be exceedingly probable.

Utrecht, Org. Chem. Labor. of the University.

(Communicated at the meeting of October 28, 1922).

Equilibria of n components in $n+1$ phases, when the quantity of one of the components approaches to zero. The influence of a new substance on an invariant equilibrium.

For the equilibrium:

$$E = F_1 + F_2 + \dots + F_{n+1} \dots \dots \dots (1)$$

of n components in $n+1$ phases, as we have seen furtherly, are valid the equations:

$$Z_i - x_i \frac{\partial Z_i}{\partial x_i} - y_i \frac{\partial Z_i}{\partial y_i} - \dots = K \dots \dots \dots (2)$$

wherein

$$i = 1, 2, \dots, (n+1)$$

and further:

$$\left. \begin{aligned} \frac{\partial Z_1}{\partial x_1} = \frac{\partial Z_2}{\partial x_2} = \dots = \frac{\partial Z_{n+1}}{\partial x_{n+1}} = K_x \\ \frac{\partial Z_1}{\partial y_1} = \frac{\partial Z_2}{\partial y_2} = \dots = \frac{\partial Z_{n+1}}{\partial y_{n+1}} = K_y \end{aligned} \right\} \dots \dots \dots (3)$$

to which still must be added the corresponding equations for the variables $z_1, z_2, \dots, u_1, u_2, \dots$ etc. As it is apparent from the number of equations (viz. $n^2 + n$) and the number of variables (viz. $n^2 + n + 1$), this equilibrium is monovariant, consequently, in the P, T -diagram we represent it by a curve, which we call E .

When in this equilibrium E all phases with constant composition contain together only $n-1$ of the n components, so that in these phases one of the components f.i. X is missing, then, in the phases with variable composition the quantity of this component X may approach to Zero.

Then the equilibrium E passes into an equilibrium, that we call $E(x=0)$ which consists of $n-1$ components in $n+1$ phases and that, consequently is invariant; in the P, T -diagram it is represented therefore, by a point which we shall call $i(x=0)$. This point is the invariant terminating — or beginning — point of curve E .

As we do approach the quantity of the component X to zero, we put again:

$$Z_1 = Z'_1 + RTx_1 \log x_1 \quad Z_2 = Z'_2 + RTx_2 \log x_2 \quad . \quad (4)$$

etc. In similar way as we have done formerly, now we find:

$$H_i dT - V_i dP + RTx_i + y_i d\left(\frac{\partial Z'}{\partial y}\right)_i + \dots = -dK \quad . \quad (5)$$

$$i = 1, 2, \dots (n+1)$$

$$x_2 = \mu_2 x_1 \quad x_3 = \mu_3 x_1 \dots x_{n+1} = \mu_{n+1} x_1 \quad . \quad . \quad (6)$$

$$d\frac{\partial Z'_1}{\partial y_1} = d\frac{\partial Z'_2}{\partial y_2} = \dots = d\frac{\partial Z'_{n+1}}{\partial y_{n+1}} = dK_y \quad . \quad . \quad (7)$$

To these equations (7) must be added the corresponding equations for the variables $z_1, z_2, \dots u_1, u_2$. The sign d indicates that there must be differentiated with respect to all variables.

Now we add to one another the $n+1$ equations (5) after having multiplied the first with λ_1 , the second with λ_2 , etc. Then we obtain:

$$\left. \begin{aligned} \Sigma(\lambda H) \cdot dT - \Sigma(\lambda V) \cdot dP + RT \Sigma(\lambda x) + \Sigma(\lambda y) dK_y + \\ + \Sigma(\lambda z) \cdot dK_z + \dots = - \Sigma(\lambda) \cdot dK \end{aligned} \right\} \quad . \quad (8)$$

Now we put:

$$\left. \begin{aligned} \Sigma(\lambda) &= 0 \quad \text{of} \quad \lambda_1 + \lambda_2 + \dots + \lambda_{n+1} = 0 \\ \Sigma(\lambda x) &= 0 \quad \text{of} \quad \lambda_1 x_1 + \lambda_2 x_2 + \dots + \lambda_{n+1} x_{n+1} = 0 \\ \Sigma(\lambda y) &= 0 \quad \text{of} \quad \lambda_1 y_1 + \lambda_2 y_2 + \dots + \lambda_{n+1} y_{n+1} = 0 \end{aligned} \right\} \quad . \quad (9)$$

etc. but *not* $\Sigma(\lambda H)$ and $\Sigma(\lambda V)$.

Then we have n equations, so that that the n ratio's between $\lambda_1, \lambda_2, \dots \lambda_{n+1}$ are defined. The reaction:

$$\lambda_1 F_1 + \lambda_2 F_2 + \dots + \lambda_{n+1} F_{n+1} = 0 \quad . \quad . \quad . \quad (10)$$

which may occur in the monovariant equilibrium E , when the quantity of the component X is infinitely small, is, therefore, also defined. We shall call this equilibrium, which differs extremely little from $E(x=0)$ the equilibrium E (*Lim* $x=0$) or shortly the equilibrium $E(x)$. With the aid of (9) now (8) passes into:

$$\left(\frac{dP}{dT}\right)_x = \frac{\Sigma(\lambda H)}{\Sigma(\lambda V)} \quad . \quad . \quad . \quad . \quad . \quad (11)$$

wherein λ_1, λ_2 are defined by (9).

Consequently the direction of the tangent to curve E in its invariant point of beginning or terminating $i(x=0)$ is defined by (11). The relation (7) (XIX) is, therefore, true also when the quantity of one of the components approaches to zero.

phases is defined by (6). By (13) is defined whether the temperature is rising or falling; by (15) is defined whether the pressure is increasing or decreasing.

We write the isovolumetrical reaction:



wherein all reaction-coefficients have been taken positive. Now we have:

$$\Sigma (\lambda H)_V = \lambda_q H_q + \lambda_{q+1} H_{q+1} + \dots - \lambda_1 H_1 - \lambda_2 H_2 - \dots$$

$$\Sigma (\lambda x)_V = \lambda_q x_q + \lambda_{q+1} x_{q+1} + \dots - \lambda_1 x_1 - \lambda_2 x_2 - \dots$$

Now we assume that we have written reaction (17) in such a way that it proceeds on addition of heat from the left to the right; consequently $\Sigma (\lambda H)_V$ is positive. In order to determine the sign of $\Sigma (\lambda x)_V$ we have to dissolve $\lambda_1 \lambda_2 \dots$ from (12) and we must know the partition of the new substance between the different phases; this may be found from (6).

In some cases the sign of $\Sigma (\lambda x)_V$ is known, however, at once without this calculation. When f.i. the new substance occurs only in one or more of the phases, which arise in (17) on addition of heat, consequently in $F_q F_{q+1} \dots$, then is $x_1 = 0, x_2 = 0 \dots x_{q-1} = 0$ and, therefore $\Sigma (\lambda x)_V$ is positive. It follows then from (13) that $(dT)_x$ is negative.

When, however, the new substance occurs only in one or more of the phases, which arise in (17) on withdrawing heat, then $x_q x_{q+1} \dots$ are zero, so that $\Sigma (\lambda x)_V$ is negative. Then it follows from (13) that $(dT)_x$ is positive.

When, however, the new substance occurs in both groups of phases, then only a calculation more in detail may decide on the sign of $\Sigma (\lambda x)_V$ and consequently also on the sign of $(dT)_x$.

Now we represent the isentropical reaction also by



However we have to take in mind, that $\lambda_1 \lambda_2 \dots$ in this case, must not be dissolved from (12) but from (14). Consequently in (18) $\lambda_1 \lambda_2 \dots$ shall have not only other values than in (17), but one or more of them may have also other signs, so that they must be transferred from the one part to the other. Now we have:

$$\Sigma (\lambda V)_H = \lambda_q V_q + \lambda_{q+1} V_{q+1} + \dots - \lambda_1 V_1 - \lambda_2 V_2 - \dots$$

$$\Sigma (\lambda x)_H = \lambda_q x_q + \lambda_{q+1} x_{q+1} + \dots - \lambda_1 x_1 - \lambda_2 x_2 - \dots$$

Now we assume that reaction (18) is written in such a way that it is proceeding from left to right with increase of volume. Consequently $\Sigma (\lambda V)_H$ is positive. When the new substance occurs only

in one or more of the phases which arise at increase of volume, then $\Sigma(\lambda x)_H$ is positive and, in accordance with (15) therefore also $(dP)_x$.

When, however, the new substance occurs only in one or more of the phases which arise on decrease of volume, then $\Sigma(\lambda x)_H$ is negative and therefore, also $(dP)_x$ is negative.

Hence we may deduce the following rules:

When we add a new substance to an invariant equilibrium $E(x=0)$ then a monovariant equilibrium E occurs, which we represent in a P, T -diagram by a curve E ; when the new substance occurs only in one or more of the phases, which arise at the isovolumetrical reaction on addition (withdrawal) of heat, then the temperature is lowered (raised); consequently curve E proceeds starting from its invariant beginning-point towards higher (lower) pressures.

In some cases we may also deduce something on the direction of curve E in its invariant beginning-point in the following way. We assume that the new substance which is added to the invariant equilibrium:

$$E(x=0) = F_1 + F_2 + \dots + F_q + F_{q+1} + \dots + F_{n+1}$$

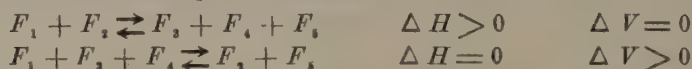
occurs only in the phases $F_{q+1} \dots F_{n+1}$ and, therefore, not in F_1, F_2, \dots, F_q . This is surely the case when $F_1 \dots F_q$ are phases of constant composition. When we take away from the equilibrium E the phases $F_{q+1} \dots F_{n+1}$, then we keep an plurivariant equilibrium $F_1 \dots F_q$; this is represented in the P, T -diagram by a plurivariant region. As curve E must be situated in this region, hence follows the said-above. In the special case that the new substance occurs in one of the phases only, curve E coincides, therefore, with one of the monovariant equilibria of the equilibrium $E(x=0)$.

Before applying those considerations to some cases, firstly I will draw the attention to some points, which have been already discussed before. When we know of the isovolumetrical and isentropical reaction the ratio of the coefficients $\lambda_1, \lambda_2, \dots$ and also in which direction those reactions proceed on addition of heat or on increase of volume, then we shall say that those reactions are known quantitatively. When we know, however, only the signs of $\lambda_1, \lambda_2, \dots$ and also in which direction the reactions are proceeding on addition of heat or on increase of volume, then we shall say that the reactions are known qualitatively. Then we only know which phases are at the one side and which at the other side of the reaction-sign.

When we know of each phase of the invariant equilibrium $E(x=0)$ the entropy, the volume and the composition, then with the aid of (12) and (14) we may define the isovolumetrical and isentropical reaction quantitatively. Consequently we are able to draw exactly the direction of the different monovariant curves in the P, T -diagram, we call it a quantitative P, T -diagram.

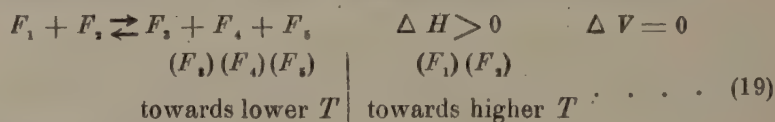
When we only know both reactions qualitatively, then we can define only whether the monovariant curves proceed, starting from the invariant point towards higher or lower temperatures and towards higher or lower pressures; but then their situation with respect to one another is still undefined; this we call a qualitative P, T -diagram.

We take for example the reactions:

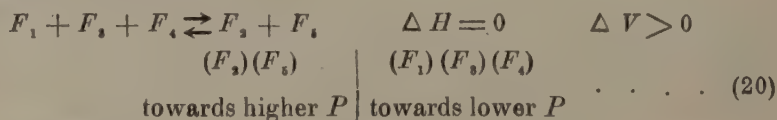


of a ternary invariant equilibrium. The first is, according to the supposition $\Delta V = 0$, the isovolumetrical reaction and it takes place, according to the supposition $\Delta H > 0$ from left to right on addition of heat. It appears from $\Delta H = 0$ and $\Delta V > 0$ that the second one is the isentropical reaction and that the volume increases from left to right.

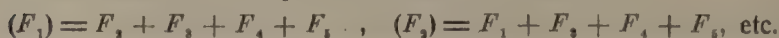
In accordance to our former considerations, now we have:



Further we have:



In accordance to our previous notation, herein is:



Now we know qualitatively the P, T -diagram; we know viz. that from the invariant point curve (F_1) is going towards higher T and lower P ; curve (F_2) goes towards higher T and at the same time towards higher P , etc.

Inversely we can also find from a qualitative P, T -diagram the qualitative isovolumetrical and isentropical reaction. When we know f.i. that the curves (F_1) and (F_2) go towards higher temperatures and (F_3) (F_4) and (F_5) towards lower temperatures, then we have to construe (19) in the inverse direction viz. from the bottom to the top, in order to find the isovolumetrical reaction.

When we know that (F_2) and (F_3) go towards higher temperatures, and (F_1) (F_3) and (F_4) towards lower pressures, then we find at once, by construing (20) in the inverse direction the isentropical reaction.

Firstly we shall apply those considerations to a simple case viz. to the addition of a new substance to the invariant unary equilibrium $E(x=0) = F + L + G$. The P, T -diagram may belong to two types, viz. when the volume decreases, on melting of the solid substance, then fig 1 is true; when the volume increases, then fig 2 is valid. The regions in which occur the phases F, L and G are indicated by the same letters, but in a circle; the curves are represented by (F) , (L) and (G) ; in accordance with our notation is $(F) = L + G$, etc.

When we add to $E(x=0)$ a new substance, which occurs only in the liquid, then the monovariant equilibrium $E = F + L + G$ arises; when we take away from it L , then we keep the equilibrium $F + G = (L)$.

Curve E coincides therefore in figs 1 and 2 with curve (L) of the invariant unary equilibrium $E(x=0)$.

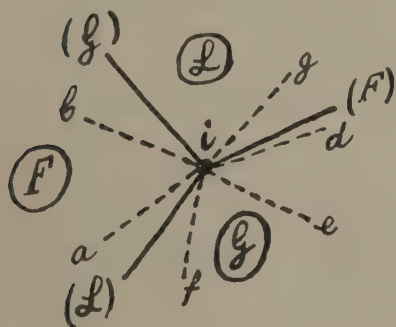


Fig. 1.

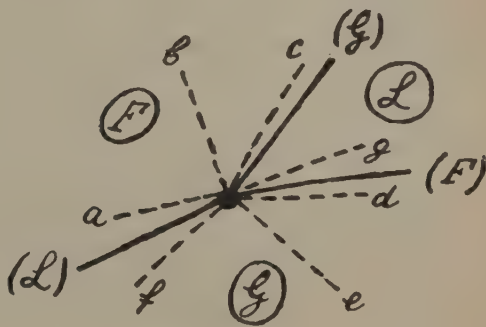


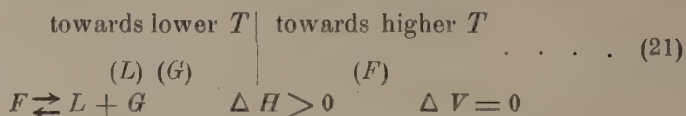
Fig. 2.

When we add a volatile substance, then we must take away from the monovariant equilibrium the phases L and G , so that we keep F only. Therefore, curve E must be situated in the region F , as f. i. ia , ib and ic in the figs 1 and 2.

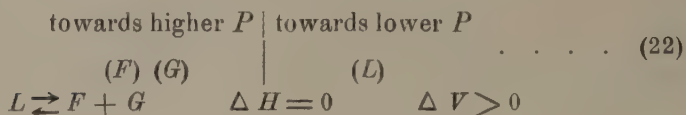
When we add a substance, which is not volatile, which gives, however, mixed-crystals with F , then we must take away from the equilibrium E the phases F and L , so that the vapour G only remains. Therefore, curve E must be situated in the region G .

We may obtain also these results by using the qualitative iso-volumetrical and isentropical reaction, which we can deduce easily

from the figs 1 and 2. It follows from the position of the curves in fig 1.



and



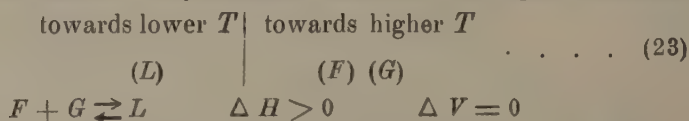
so that both reactions are known qualitatively.

Now we add to this equilibrium $E(x=0) = F + L + G$ a substance, which occurs in the liquid only. As in the isovolumetrical reaction (21) L is placed at the right side of the reaction-sign, consequently, in accordance with our rules, T is lowered; as in the isentropical reaction (22) L is placed at the left side of the reaction-sign, the pressure is also lowered, therefore.

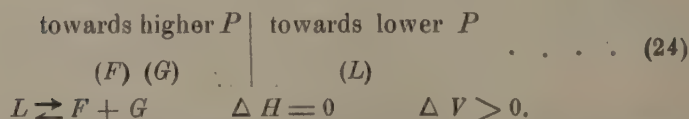
Consequently in fig. 1 curve E proceeds starting from point i towards lower T and P ; this is in accordance with the deduced above, that curve E coincides with curve (L) in this case.

When we add a volatile substance, than it occurs in L and G . As both those phases are placed in (21) at the right side of the reaction-sign, consequently T is lowered. As L and G are placed in (22) at different sides of the reaction-sign, the pressure may be as well increased as decreased. Therefore, curve E may be represented by ia or ib in fig. 1. Which of these curves may occur in a definite case, cannot be deduced in this manner; we are able to do this, as we shall see further, with the aid of the quantitative reactions.

In order to deduce the qualitative reactions from fig. 2, we write:



and



When we add a new substance, which occurs in L and G , then we find that curve E may be represented in fig. 2 by ia , ib or ic .

It is apparent from the previous that by simple considerations we may deduce already something about the direction of curve E from the qualitative P, T -diagram of an invariant equilibrium $E(x=0)$.

When, however, we know the quantitative reactions, then we are able to deduce not only the quantitative P, T -diagram for the equilibrium $E(x=0)$ but also $(dT)_x$ and $(dP)_x$ for the equilibrium E and consequently we can define exactly the direction of curve E .

When we represent entropy and volume of F by H and V , of L by H_1 and V_1 and of G by H_2 and V_2 , and when we assume that the substance melts on decrease of volume, then we have:

$$H_2 > H_1 > H \quad \text{and} \quad V_2 > V > V_1 \quad \dots \quad (25)$$

We write the isovolumetrical reaction:

$$F + \lambda_1 L + \lambda_2 G = 0 \quad \dots \quad (26)$$

As, in accordance with (12):

$$1 + \lambda_1 + \lambda_2 = 0 \quad \text{and} \quad V + \lambda_1 V_1 + \lambda_2 V_2 = 0 \quad \dots \quad (27)$$

it follows:

$$\lambda_1 = -\frac{V_2 - V}{V_2 - V_1} \quad \text{and} \quad \lambda_2 = -\frac{V - V_1}{V_2 - V_1} \quad \dots \quad (28)$$

so that λ_1 and λ_2 are both negative. Instead of (26) we now write:

$$F \rightleftharpoons \lambda_1 L + \lambda_2 G \quad \dots \quad (29)$$

wherein

$$\lambda_1 = \frac{V_2 - V}{V_2 - V_1} \quad \text{and} \quad \lambda_2 = \frac{V - V_1}{V_2 - V_1} \quad \dots \quad (30)$$

and

$$\Sigma (\lambda H)_V = \lambda_1 H_1 + \lambda_2 H_2 - H \quad \dots \quad (31)$$

Now we may prove that $\Sigma (\lambda H)_V$ is generally positive, so that, on addition of heat the isovolumetrical reaction (29) proceeds from left to right.

In a similar way we find for the isentropical reaction:

$$\mu_1 L \rightleftharpoons F + \mu_2 G \quad \dots \quad (32)$$

and

$$\Sigma (\lambda V)_H = V + \mu_2 V_2 - \mu_1 V_1$$

wherein

$$\mu_1 = \frac{H_1 - H}{H_2 - H_1} \quad \text{en} \quad \mu_2 = \frac{H_1 - H}{H_2 - H_1} \quad \dots \quad (33)$$

so that μ_1 and μ_2 are both positive.

As $\Sigma (\lambda V)_H$ is positive, reaction (32) proceeds from left to right with increase of volume.

With the aid of reactions (29) and (32), as is discussed in previous communications we now can deduce the P, T -diagram quantitatively; then we find fig. 1.

Now we add a new substance which occurs in the liquid only.

When we call its concentration x_1 , then we have:

$$\Sigma (\lambda x)_V = \lambda_1 x_1 \text{ and } \Sigma (\lambda x)_H = -\mu_1 x_1$$

so that, in accordance with (13) and (15):

$$(dT)_x = \frac{-RT \lambda_1 x_1}{\Sigma (\lambda H)_V} \text{ and } (dP)_x = \frac{-RT \mu_1 x_1}{\Sigma (\lambda V)_H} \quad . \quad . \quad (34)$$

Consequently in fig. 1 curve E proceeds, starting from point i towards lower P and T .

It follows from (33):

$$\left(\frac{dP}{dT}\right)_x = \frac{\mu_1}{\lambda_1} \cdot \frac{-H + \lambda_2 H_2 + \lambda_1 H_1}{V + \mu_2 V_2 - \mu_1 V_1} = \frac{H_2 - H}{V_2 - V} \quad . \quad . \quad (35)$$

Hence it appears that in fig. 1 curve E coincides with curve (L) . Also we may find (34) at once with the aid of (9) and (11). We put viz.:

$$\Sigma (\lambda) = 1 + \lambda_1 + \lambda_2 = 0 \text{ and } \Sigma (\lambda x) = \lambda_1 x_1 = 0$$

so that $\lambda_1 = 0$ and $\lambda_2 = -1$. Hence it follows:

$$\Sigma (\lambda H) = H - H_2 \text{ and } \Sigma (\lambda V) = V - V_2,$$

consequently for (11) the same value as in (34).

When the new substance occurs in liquid and vapour with the concentrations x_1 and x_2 , then we have:

$$\text{in accordance with (29):} \quad \Sigma (\lambda x)_V = \lambda_1 x_1 + \lambda_2 x_2$$

$$\text{and in accordance with (32):} \quad \Sigma (\lambda x)_H = -\mu_1 x_1 + \mu_2 x_2$$

so that $(dT)_x$ and $(dP)_x$ are known again. We see that $(dT)_x$ is negative, but that $(dP)_x$ may be as well positive as negative. Curve E , therefore, may be situated in fig. 1 as ia or ib .

When we put:

$$\frac{\mu_2}{\mu_1} = \frac{H_2 - H}{H_1 - H} = K \quad . \quad . \quad . \quad . \quad . \quad (36)$$

then is

$$\Sigma (\lambda x)_H = \mu_1 (x_2 - K x_1) \quad . \quad . \quad . \quad . \quad . \quad (37)$$

wherein, in accordance to (35), $K > 1$.

Now we find:

for $\frac{x_2}{x_1} > K$ is $(dP)_x > 0$; consequently curve E goes, starting from point i towards higher pressures;

for $\frac{x_2}{x_1} < K$ is $(dP)_x < 0$; consequently curve E goes, starting from point i towards lower pressures.

When f.i. is $K=5$, then the concentration of the new substance in the vapour must be at least five times as large as in the liquid, that curve E is proceeding towards higher pressures, starting from i .

In order to define the direction of curve E we define the values of λ_1 and λ_2 according (9) from:

$$1 + \lambda_1 + \lambda_2 = 0 \quad \text{and} \quad \lambda_1 x_1 + \lambda_2 x_2 = 0$$

(11) then passes into:

$$\left(\frac{dP}{dT}\right)_x = \frac{x_2 (H_1 - H) - x_1 (H_2 - H)}{x_2 (V_1 - V) - x_1 (V_2 - V)} \quad \dots \quad (38)$$

by which the direction of curve E is defined. This direction, as follows from (37), is dependent on the partition $(x_2: x_1)$ of the new substance between gas and liquid. Also it follows from (37) that curve E must be situated between the curves (L) and (G) .

We now add a new substance which forms mixed-crystals with F , but which does not occur in the vapour. When we represent its concentration in F and L by x and x_1 then it follows from (29) and (32):

$$\Sigma (\lambda x)_V = \lambda_1 x_1 - x \quad \text{and} \quad \Sigma (\lambda x)_H = x - \mu_1 x_1$$

consequently:

$$(dT)_x = \frac{RT(x - \lambda_1 x_1)}{\Sigma (\lambda H)_V} \quad \text{and} \quad (dP)_x = \frac{RT(x - \mu_1 x_1)}{\Sigma (\lambda V)_H} \quad \dots \quad (39)$$

It is apparent from (30) and (33) that $\lambda_1 < 1$ and $\mu_1 > 1$, but also that λ_1 differs very little only from 1. It follows from (39):

$$\text{for } \frac{x}{x_1} > \mu_1 \text{ is } (dT)_x > 0 \text{ and } (dP)_x > 0;$$

Curve E is situated then, f.i. like curve id in fig. 1

$$\text{for } \mu_1 > \frac{x}{x_1} > \lambda_1 \text{ is } (dT)_x > 0 \text{ and } (dP)_x < 0;$$

Curve E is then situated, f.i. like curve ie in fig. 1

$$\text{for } \frac{x}{x_1} < \lambda_1 \text{ is } (dT)_x < 0 \text{ and } (dP)_x < 0;$$

Curve E then is situated f.i. as curve if in fig. 1.

In order to define the direction of curve E we take in accordance with (9):

$$\Sigma (\lambda) = 1 + \lambda_1 + \lambda_2 = 0 \quad \text{and} \quad \Sigma (\lambda x) = x + \lambda_1 x_1 = 0.$$

With the values of λ_1 and λ_2 which follow from this we find for (11):

$$\left(\frac{dP}{dT}\right)_x = \frac{x_1 (H_2 - H) - x (H_2 - H_1)}{x_1 (V_2 - V) - x (V_2 - V_1)} \quad \dots \quad (40)$$

so that the direction of curve E is defined.

Also it is apparent from (39) that E must be situated between the curves (F) and (L).

Finally we shall assume that the new substance divides itself over the three phases, we call its concentration in F L and G x_1 and x_2 . We now have according to (29) and (32):

$\Sigma (\lambda x)_V = -x + \lambda_1 x_1 + \lambda_2 x_2$ and $\Sigma (\lambda x)_H = x - \mu_1 x_1 + \mu_2 x_2$ wherein $\lambda_1 + \lambda_2 = 1$ and $\mu_1 = 1 + \mu_2$, so that $(dT)_x$ and $(dP)_x$ are known.

We now put:

$$\Sigma (\lambda x)_V = r \text{ and } \Sigma (\lambda x)_H = s \quad . \quad . \quad . \quad . \quad . \quad (41)$$

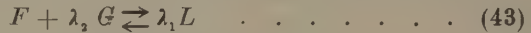
As we are able to satisfy (40), independent on the values of r and s , by positive values of x x_1 and x_2 , it follows that curve E may go in every direction starting from point i . It may be situated, therefore, not only in one of the regions F and G , but also, like f. i. curve ig , in the region L . Of course its situation is dependent on the partition of the new substance between the three phases.

The same considerations as for fig 1 are also valid for fig 2, for this we have to examine however more in detail the occurrence of curve ic .

Instead of (25) we have for fig 2:

$$H_2 > H_1 > H \text{ and } V_2 > V_1 > V \quad . \quad . \quad . \quad . \quad . \quad (42)$$

As λ_2 is negative now, in accordance with (30) the isovolumetrical reaction passes into:



wherein:

$$\lambda_1 = \frac{V_2 - V}{V_2 - V_1} \text{ and } \lambda_2 = \frac{V_1 - V}{V_2 - V_1}$$

so that

$$\Sigma (\lambda H) = \lambda_1 H_1 - H - \lambda_2 G$$

is generally positive; reaction (43) is proceeding therefore, on addition of heat from left to right.

When we now add a new substance, which occurs in liquid and vapour, then we have: $\Sigma (\lambda x)_V = \lambda_1 x_1 - \lambda_2 x_2$. In order that $(dT)_x$ is positive, $\Sigma (\lambda x)_V$ must be negative, consequently:

$$\frac{x_2}{x_1} > \frac{\lambda_1}{\lambda_2} \quad \text{or} \quad \frac{x_2}{x_1} > \frac{V_2 - V}{V_1 - V} \quad . \quad . \quad . \quad . \quad . \quad (44)$$

As in general $V_2 - V$ is some thousand times larger than $V_1 - V$ curve ic therefore can, occur only in the very special case that the concentration of the new substance is some thousand times larger in the vapour than in the liquid.

We may summarize some of the previous deductions in the following way.

When we add a new substance to an invariant unary equilibrium $E(x=0) = F + L + G$, then an equilibrium $E = F + L + G$ arises that is represented in the P, T -diagram by a curve E ; this curve begins in the invariant point i of the equilibrium $E(x=0)$.

When the new substance occurs in the liquid only, then curve E coincides with curve $(L) = F + G$ of the system $E(x=0)$.

When the new substance is occurring in liquid and vapour then curve E is situated in the region H' ; its direction is defined by the partition of the new substance between vapour and liquid. A curve, like ic in fig. 2 may, however, occur only in very special circumstances.

When the new substance is occurring in liquid and solid phase (consequently with formation of mixed crystals) then curve E is situated in the region G ; its direction is defined by the partition of the new substance between mixed crystals and liquid.

When the new substance occurs in the three phases, then curve E may be situated in each of the three regions; its direction is defined by the partition of the new substance between the three phases.

(To be continued).

Leiden, Lab. of Inorganic Chemistry.

Mathematics. — *“Ueber Determinanten aus Formenkoeffizienten”.*

By B. L. VAN DER WAERDEN. (Communicated by Prof. L. E. J. BROUWER).

(Communicated at the meeting of October 28, 1922).

§ 1. *Die Aufgabe.*

Vier binäre Bilinearformen $(ax)(a'x')$ bestimmen die Determinante

$$\Delta = \begin{vmatrix} 1_{1,1} & 1_{1,2} & 1_{2,1} & 1_{2,2} \\ \vdots & & & \\ 4_{1,1} & & & \end{vmatrix}$$

(wo $1_{i,k}$ die Koeffizienten der ersten Form sind, usw.), welche invariant ist gegenüber unabhängigen linearen Transformationen der beiden binären Gebiete x und x' , weil bei diesen Transformationen auch die Koeffizientenreihen linear transformiert werden.

Sechs lineare Komplexe im dreidimensionalen Raum R haben ebenso eine Invariante

$$\Delta = \begin{vmatrix} 1_{12} & 1_{13} & 1_{14} & 1_{34} & 1_{42} & 1_{23} \\ \vdots & & & & & \\ 6_{12} & & & & & \end{vmatrix}.$$

Für das Problem: Derartige Invarianten symbolisch darzustellen, werde ich im Folgenden eine allgemeine Methode angeben und diese dann auf die genannten zwei Beispiele anwenden.

§ 2. *Lemma.*

Wenn eine Form f in n n -ären Veränderlichen (eine n -äre Veränderliche ist ein Inbegriff von n homogenen Grössen $x_1 \dots x_n$), sich gegenüber Permutation dieser Veränderlichen verhält wie eine alternierende Funktion, so enthält sie entweder den Klammerfaktor $(xy \dots)$, oder sie verschwindet identisch.

Beweis. Setzt man zwei der Veränderlichen einander gleich, so verschwindet f identisch, da dann $f = -f$ wird. Wenn man dann nach dem Gleichsetzen mit Polarenprozessen operiert, so erhält man immer wieder identisch Null. Also verschwindet das erste Glied der GORDAN-CAPELLI-schen Reihenentwicklung der Form f identisch. Alle weiteren Glieder aber enthalten entweder den Faktor $(xy \dots)$, oder verschwinden. Daraus folgt das Lemma.

Bemerkung. Für den Fall (den ich eben benötige), wo die x, y, \dots in f linear auftreten, ist das Lemma elementarer zu beweisen. Es ist dann nämlich symbolisch

$$f = A \cdot (a' x) (b' y) \dots$$

Vertauscht man x, y, \dots in allen möglichen Weisen, und addiert mit \pm , so kommt

$$n! f = A \begin{vmatrix} (a' x) (a' y) \dots \\ (b' x) (b' y) \dots \\ \vdots \\ \vdots \end{vmatrix},$$

oder nach dem Multiplikationssatze der Determinanten

$$n! f = A \cdot (a' b' \dots) (x y \dots)$$

$$f = \frac{A}{n!} (a' b' \dots) (x y \dots).$$

§ 3. Die allgemeine Methode.

Es seien gegeben N Formen derselben Art, mit je N Koeffizienten. Ich setze voraus, dass man alle Invarianten vom 1. Grade in den Koeffizienten dieser Formen, symbolisch hingeschrieben hat. Verlangt wird dann, die Determinante Δ der N^2 Koeffizienten durch diese Invarianten auszudrücken. Lösung: Man stelle aus diesen Invarianten irgendeine alternierende Funktion der Koeffizientenreihen her. Wenn diese nicht identisch verschwindet, so stellt sie nach dem Lemma bis auf einen konstanten Faktor die gesuchte Determinante Δ dar.

In manchen Fällen gelingt das Auffinden einer solchen alternierenden Funktion sogleich. Ist dies nicht der Fall, so kann man so verfahren: Man wähle irgendeine lineare Invariante I des Systems, und bilde

$$\sum \pm I$$

unter Vertauschung der Formen in allen möglichen Weisen. Es gibt wegen der Existenz von Δ sicher mindestens eine Invariante I , für welche diese Bildung nicht identisch verschwindet, und die Bildung stellt dann nach § 2, weil sie alterniert, bis auf einen konstanten Faktor die gesuchte Invariante Δ dar.

§ 4. Erstes Beispiel. Vier Bilinearformen in zwei unabhängigen binären Veränderlichen.

Die Invarianten der Formen $(1x)(1'x'), \dots, (4x)(4'x')$ gehören den

folgenden Typen an:¹⁾

$$\begin{cases} B_{12} = (12)(1'2') = B_{21} \\ F_{1234} = (12)(2'3')(34)(4'1') = F_{3412} = F_{4321} = F_{2143} \end{cases}$$

Die Invarianten vom 1. Grade in den Koeffizienten der 4 Formen sind also:

$$\begin{cases} B_{12} B_{34}, B_{13} B_{24}, \text{ usw.} \\ F_{1234}, \text{ usw.} \end{cases}$$

Nun ist

$$\Sigma \pm B_{12} B_{34} \equiv 0$$

es bleibt also für Δ nur die Möglichkeit:

$$\begin{aligned} \Delta &= A \cdot \Sigma \pm F_{1234} \\ &= 4A \cdot \{ F_{1234} - F_{1234} - F_{1324} + F_{1423} + F_{1342} - F_{1432} \}. \end{aligned}$$

Zur Bestimmung der Konstanten A genügt das Zahlenbeispiel

$$\Delta = \begin{vmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & & \\ & & & \\ & & & \end{vmatrix}.$$

Das gibt

$$A = -\frac{1}{12}.$$

Um nun $\Sigma \pm F_{1234}$ in seiner einfachsten Form darzustellen, verwenden wir die sich aus

$$(2'3')(4'1') = (2'4')(3'1') + (1'2')(3'4')$$

ergebende Identität

$$F_{1234} = -F_{1243} + B_{12} B_{34}$$

Diese erlaubt uns, zwei beliebige F_{iklm} aufeinander zu reduzieren (durch wiederholtes Vertauschen von aufeinanderfolgenden Indizes). So reduzieren wir die letzten fünf Glieder der angeschriebenen Entwicklung für Δ auf das erste. Es kommt schliesslich

$$\Delta = -2F_{1234} + B_{12} B_{34} - B_{13} B_{24} + B_{14} B_{23}.$$

Wenn man will, kann man auch schreiben

$$\Delta = -F_{1234} + F_{2341}.$$

§ 5. Zweites Beispiel. Sechs lineare Komplexe im Quaternären.

Geschrieben in WEITZENBÖCK—WAEELSCH'schen Komplexsymbolen²⁾, sind alle Invarianten von linearen Komplexen reduzibel auf „Ketten“, wie

¹⁾ Da die beiden binären Gebiete unabhängig transformiert werden, so bestehen die Invarianten aus Klammerfaktoren, deren Symbole beide demselben Gebiete angehören.

²⁾ Siehe R. WEITZENBÖCK, Komplex-Symbolik, Leipzig 1908, WAEELSCH, Wiener Berichte Dec. 1889, oder besser den III. Abschnitt der in Kurzem bei Noordhoff Groningen erscheinenden „Invariantentheorie“ von R. WEITZENBÖCK.

$$[12'] = (1'2)(21') = (1'2)^2 = [21'] \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\begin{aligned} [12'34'56'] &= (12')(2'3)(34')(4'5)(56')(6'1) = [34'56'12'] = \\ &= [56'12'34'] = [16'54'32'] = \text{etc.} \end{aligned} \quad \left. \vphantom{[12'34'56']} \right\} . \quad (2)$$

Die Viererkette ist reduzibel¹⁾, vermöge *)

$$[12'34'] = \frac{1}{4} \{ [12'] [34'] - [13'] [24'] + [14'] [23'] \} \quad . \quad . \quad (3)$$

Zwei Sechserketten die auseinander entstehen durch Vertauschen zweier aufeinanderfolgender Indizes, sind zueinander reduzibel vermöge der Identität *)

$$(xp')(p'q)(qu') + (xq')(q'p)(pu') = -\frac{1}{2} [pq'] (u'y),$$

zufolge welcher

$$[12'34'..] + [13'24'..] = -\frac{1}{2} [23'] [14'..] \quad . \quad . \quad . \quad (4)$$

und dual dazu. Aus (3) und (4) folgt noch

$$\begin{aligned} [12'34'56'] &- [13'24'56'] - \frac{1}{8} [23'] \{ [14'] [56'] - [15'] [46'] + [16'] [45'] \} \\ \text{und dual dazu} & \\ [12'34'56'] &= -[21'34'56'] - \frac{1}{8} [12'] \{ [34'] [56'] - [35'] [46'] + [36'] [45'] \} \end{aligned} \quad \left. \vphantom{[12'34'56']} \right\} (5)$$

Um nun die Invariante

$$\Delta = \begin{vmatrix} 1_{12} & 1_{13} & 1_{14} & 1_{34} & 1_{42} & 1_{23} \\ \vdots & & & & & \\ 6_{12} & & & & & \end{vmatrix}$$

symbolisch darzustellen, bemerken wir, dass

$$\Sigma \pm [12'] [34'] [56'] \equiv 0.$$

Also bleibt als einzige Möglichkeit

$$\Delta = A \cdot \Sigma \pm [12'34'56'].$$

Zur Bestimmung von A nehmen wir das Zahlenbeispiel

$$\Delta = \begin{vmatrix} 1 & 0 & . & . \\ 0 & 1 & & \\ . & & . & \\ . & & & . \end{vmatrix}$$

und erhalten

$$A = -\frac{2}{6},$$

also

$$\Delta = -\frac{2}{6!} \Sigma \pm [12'34'56'] \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Man könnte nun, so wie im vorigen §, diesen Ausdruck weiter

¹⁾ Die Sechserkette ist nicht reduzibel. Vergl. R. WEITZENBÖCK, Jahresber. D. Math.-Ver. 19 (1910) und Wiener Ber. 122 (1913).

²⁾ R. WEITZENBÖCK, Invariantentheorie III, § 5 Gl. (10).

³⁾ Komplex-Symb. p. 8, (26) und (26a); Invariantentheorie III, § 5 Gl. (4).

reduzieren mittels (5); dann aber hätte man 119 Glieder zu berechnen, und an jedem Gliede eine bis zehn Reduktionen vorzunehmen. Man weiss aber im Voraus, dass das Resultat die Form

$$\Delta = -2 [12'34'56'] + F\{[12'], \dots, [56']\} \quad . \quad . \quad . \quad (7)$$

haben muss. Wenn diese Formel gilt, so muss die duale auch gelten. Um Δ zu dualisieren, muss man $1_{1,}$ durch $1'_{1,}$, oder durch $1_{1,}$ ersetzen, usw.: Δ geht dann über in $-\Delta$. Jede Zweierkette ist zu sich selbst dual. Also kommt

$$-\Delta = -2 [1'23'45'6] + F\{[12'], \dots, [56']\} \quad . \quad . \quad . \quad (8)$$

Subtrahiert man nun (7) und (8), so fällt die Funktion F heraus, und man erhält Δ in der Form:

$$\Delta = -[12'34'56'] + [1'23'45'6] \quad . \quad . \quad . \quad . \quad (9)$$

Wenn man will, kann man für $[1'23'45'6]$ auch schreiben $[61'23'45']$, und das zweite Glied durch wiederholte Anwendung von (5) auf das erste reduzieren; es kommt schliesslich

$$\begin{aligned} \Delta = & -2 [12'34'56'] - \frac{1}{8} \{ [12'] [34'] [56'] + [23'] [45'] [61'] \} \\ & + \frac{1}{8} \{ [12'] [35'] [46'] + \text{cycl} \} \\ & - \frac{1}{8} \{ [14'] [23'] [56'] + ck \} \\ & - \frac{1}{8} \{ [14'] [26'] [35'] + ck \} \\ & + \frac{1}{8} [14'] [25'] [36'] \end{aligned} \quad \left. \vphantom{\begin{aligned} \Delta = & \end{aligned}} \right\} \quad (10)$$

wo $[..][..][..] + \text{cycl}$ bedeutet: die Summe aller Glieder, die aus dem angeschriebenen Gliede entstehen durch null- bis fünf-malige

Anwendung der Permutation $\begin{Bmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 2 & 3 & 4 & 5 & 6 & 1 \end{Bmatrix}$, während $[..][..][..] + ck$

bedeutet: die Summe aller Glieder, die aus dem angeschriebenen entstehen durch null- bis zwei-malige Anwendung der Permutation

$$\begin{Bmatrix} 12 & 34 & 56 \\ 34 & 56 & 12 \end{Bmatrix}.$$

Chemistry. — "*The dissociation constants of sulphonacetic and α -sulphonpropionic acids*". By Prof. H. J. BACKER. (Communicated by Prof. P. VAN ROMBURGH).

(Communicated at the meeting of September 30, 1922).

The α -sulphoncarboxylic acids are dibasic acids with a strong and a weak acid function.

Consequently, the free compounds belong to the strong acids, whilst the acid salts behave as weak acids.

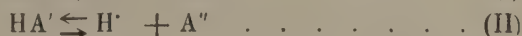
In the table the molecular conductivity of sulphonacetic and α -sulphonpropionic acid is mentioned.

When the values at an infinite dilution μ_{∞} , on account of the number of atoms in a molecule¹⁾ are taken for the sulphonacetic acid at 376, and for the sulphonpropionic acid at 373, then the mean value of the dissociation constant, at the concentrations $1/32$ and $1/64$ Grammolecule per litre, is found to be for the sulphonacetic acid 0.58 and for the sulphonpropionic acid 0.57.

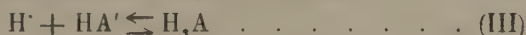
Great accuracy can not be ascribed to these figures, as the uncertainty in the determination of μ_{∞} in the case of these strong acids has a great influence on the size of the constants.

However, the values are not improbable; for WEGSCHEIDER²⁾, who has argued the validity of OSTWALD's dilution law for sulphonic acids, has calculated for benzol sulphonic, p-toluolsulphonic and β -naphthalenesulphonic acids, the constants 0.21, 0.214 and 0.267, and for the m-sulphonbenzoic acid, related to the above-mentioned acids, the constant 0.4.

In the solutions of the acid sodium salts of the sulphoncarboxylic acids chiefly the following ionic equilibria exist:



Besides, molecules of the free acid may be formed:



The conductivity of the acid sodium salts is thus caused by the ions: Na^+ , HA' , H^+ , A'' .

¹⁾ OSTWALD-LUTHER, Hand- u. Hilfsbuch 1922, 482.

²⁾ WEGSCHEIDER, Monatshefte f. Ch. 23, 340, 341 (1902); 30, 440 (1909).

Molecular conductivity at 25° C. in reciprocal Ohms¹⁾.

V (Number of liters p. G. mol.)	16	32	64	128	256	512	1024
Sulphonacetic acid $C_2H_4O_5S$	348.9	357.9	366.3	373.3	380.1	388.8	403.4
Monosodium sulphonacetate $C_2H_3O_5SNa$	88.4	98.4	110.1	123.9	141.0	163.2	191.4
Disodium sulphonacetate $C_2H_2O_5SNa_2$	162.5	180.0	194.0	206.0	215.2	223.0	228.8
Sulphonpropionic acid $C_3H_6O_5S$	345.5	355.5	362.8	369.0	373.3	379.4	387.4
Monosodium sulphonpropionate $C_3H_5O_5SNa$	82.6	91.4	101.1	112.5	126.3	146.0	169.0
Disodium sulphonpropionate $C_3H_4O_5SNa_2$	154.8	169.3	182.0	192.6	201.0	208.0	213.2
Propionanilide- α -sulphonic acid $C_9H_{11}O_4SN$	337.2	348.1	355.7	360.8	364.0	365.1	365.2
Sodium propionanilide- α -sulphonate $C_9H_{10}O_4SNNa$	63.0	66.6	69.6	71.4	73.3	74.9	76.3

In order to get an idea of the dissociation constant k_a of reaction II, the conductivity of the acid salts must be diminished by the contributions of the ions Na^+ and HA^+ .

The conductivity of the HA -ions λ_{HA^+} may, on account of the number of atoms, be estimated for the sulphonacetic acid at 36 and for the sulphonpropionic acid at 33.

Further, the dissociation degree α_1 of reaction I has to be known.

This value being not directly determinable, we may make use of BREDIG's rule²⁾, that the dissociation degree of the sodium salts of different monobasic acids rises about equally rapidly on diluting the solution.

It is therefore allowable to take the dissociation degrees sought

¹⁾ Only the conductivities of the neutral salts have been diminished by the conductivity of the water ($1.5-2.0 \times 10^{-6}$).

²⁾ BREDIG, Z. f. phys. Ch. 13, 191 (1894).

as equal to the values given by the sodium salt of an analogically built acid in the same dilution. As the properties of the acid salts of the α -sulphoncarbonic acids indicate the structure $\text{CHR}(\text{CO}_2\text{H})\text{SO}_3\text{Na}$, the sodium salt of a sulphonic acid may be chosen for the sake of comparison.

Now, with a view to determine the dissociation degree of a monobasic sulphonic acid, related to the acids in question, the anilide of sulfonpropionic acid was prepared¹⁾. The conductivity mentioned in the table shows that this propionanilide- α -sulphonic acid is a strong acid, from which it follows with certainty, that the sulphonic acid group is free and that the carboxylic group is changed into amide: $\text{CH}_3 \cdot \text{CH}(\text{CONHC}_6\text{H}_5) \cdot \text{SO}_3\text{H}$.

If μ_∞ is assumed to be 368, a value resulting from the conductivity of the sodium salts and also from the number of atoms, then the mean dissociation constant for the dilutions 64, 128 and 256 is found to be 0,39.

For the sodium salt, the conductivities at the dilutions 256, 512 and 1024, extrapolated according to BREDIG, give $\mu_\infty = 79,0$.

From this results the ionisation degree α at the dilutions v :

$v =$	16	32	64	128	256	512	1024
$\alpha =$	0,797	0,843	0,881	0,904	0,928	0,948	0,966

These values are also taken for α_1 , the dissociation degree of NaHA (reaction I).

The conductivity of the acid salt μ_{NaHA} , diminished by $\alpha_1(\lambda_{\text{Na}^+} + \lambda_{\text{HA}^-})$, will give, as a first approximation, the conductivity due to the ions H^+ and A'' .

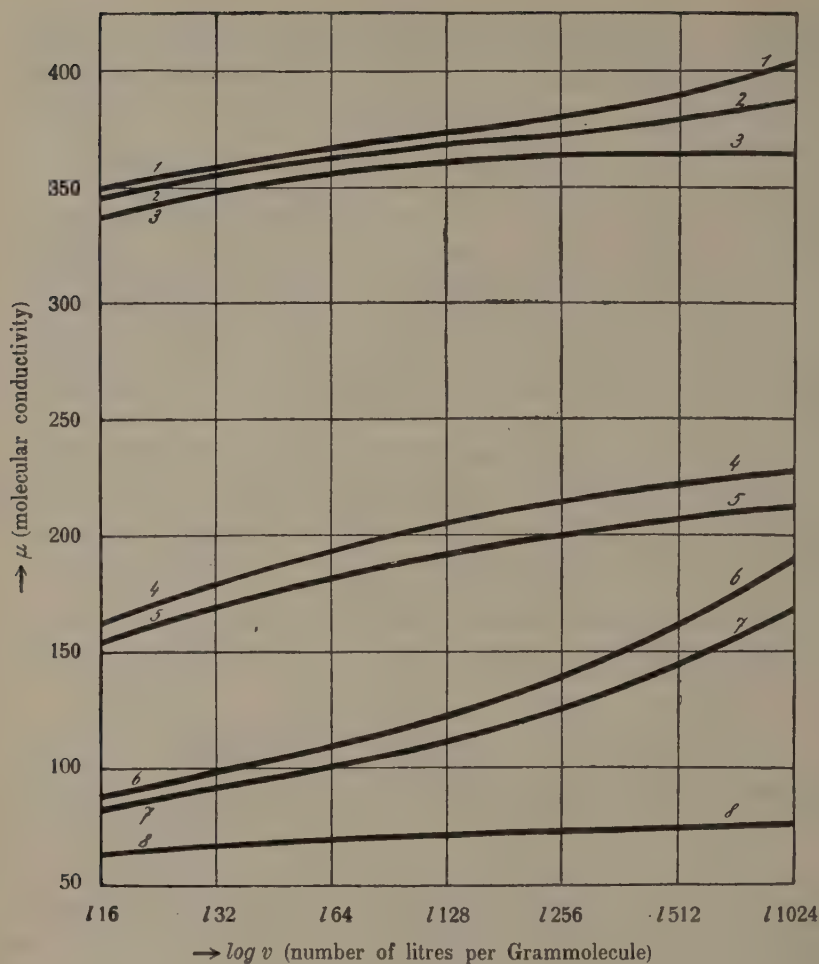
In order to get a value for k_2 , it is necessary to know the conductivity which the ions H^+ and A'' would give at a complete ionisation according to reaction II.

The equivalent conductivity of the neutral sodium salts diminished by λ_{Na^+} , gives $\lambda_{\text{A}''}$. In this way the value 72 was found for sulphonacetic acid and 65 for sulphonpropionic acid.

The conductivity of the ions H^+ and A'' at infinite dilution is then expressed by $\lambda_{\text{H}^+} + 2\lambda_{\text{A}''}$.

The observed conductivity $\mu_{\text{NaHA}} - \alpha_1(\lambda_{\text{Na}^+} + \lambda_{\text{HA}^-})$, divided by this value $\lambda_{\text{H}^+} + 2\lambda_{\text{A}''}$, gives, as a first approximation, the value of α_2 , the dissociation degree of reaction II.

¹⁾ Recueil d. tr. ch. 40, 585 (1921).



Molecular conductivity.

1. Sulphonacetic acid.
2. Sulphonpropionic acid.
3. Propionanilide- α -sulphonic acid.
4. Disodium sulphonacetate.
5. Disodium sulphonpropionate.
6. Monosodium sulphonacetate.
7. Monosodium sulphonpropionate.
8. Sodium propionanilide- α -sulphonate.

Now, a correction may be made for the fact that the concentration of the HA'-ions is smaller than agrees with reaction I,

these ions being further split up according to reaction II.

A corrected value for α_1 is obtained, from which k_1 may be calculated.

In this way k_1 is found to be for the sulphonacetic acid:

$$\begin{array}{rcccccccc} v = & 16 & 32 & 64 & 128 & 256 & 512 & 1024 \\ k_1 = & 11.3 & 10.1 & 9.2 & 8.6 & 8.0 & 7.6 & 7.3 \times 10^{-5} \end{array}$$

and for the sulphonpropionic acid:

$$\begin{array}{rcccccccc} v = & 16 & 32 & 64 & 128 & 256 & 512 & 1024 \\ k_1 = & 7.8 & 7.0 & 6.3 & 5.8 & 5.3 & 5.2 & 4.8 \times 10^{-5} \end{array}$$

The mean value of the second dissociation constant thus becomes for the sulphonacetic acid 8.9×10^{-5} and for the sulphonpropionic acid 6.0×10^{-5} .

In this statement of views no account is taken of the combination of the ions H^+ and HA' , as shown by reaction III.

A correction for this last, however, that would somewhat increase the second dissociation constant is of no value for these strongly dissociated acids, as the uncertainty in the values of the conductivity of the different ions has a greater influence.

Dr. O. RINGER and Drs. D. W. DIJKSTRA have given their assistance with some of the measurements.

A more detailed account will appear in the *Recueil d. trav. chim.*

Organic Chemical Laboratory of the University.

Groningen, 8th Sept. 1922.

Physiology. — “*On the progress of the veratrin-poisoning of the striated frog-muscle*”. By ARIE QUERIDO. (Communicated by Prof. G. VAN RIJNBEEK).

(Communicated at the meeting of October 28, 1922.)

1. *Concentration and dose.*

The nature of the action of veratrin on the striated muscular tissue still has not been sufficiently revealed, partly because of the lack of knowledge of the conditions, associating the poisoning. Repeatedly we read with various authors the remark, how fickle and incalculable the veratrin-phenomenon is in its appearance, seemingly independent of the quantity of poison used and the time it could act. It is true in 1904 MOSTINSKY¹⁾ examined the factors cooperating in the formation of a definite shape of curve and he succeeded in ascertaining the conditions incidental to this; the modifications however of these conditions in the course of an experiment, i.e. the alterations during the poisoning of the balance between muscle-metabolism and poison-action of which the curve is a result, are unknown as yet. Closely connected with this is the question, in what way the shape of the curve corresponds with the rate of poisoning of the muscle. On this subject we have some information, that is two types of contraction-shape are distinguished, viz. the type with two and with one top (fusion type), the latter of which corresponds to a stronger rate of poisoning (BOEHM²⁾, DEELMAN³⁾).

In order to study these questions further, I irritated muscle-nerve-preparations, after their immersion in a veratrin-Ringer-solution, by induction-shocks with so long a pause between the stimulations, that the influence of a contraction on the following need not be taken into account (three minutes).

In this way I collected a great number of curves of veratrin-poisonings for different concentrations of the poison. On contemplating the modifications in the veratrinogram, we can get an idea of the relation between curve and rate of poisoning, for if a poisoning is seen to progress in the direction of a diminishing or vanishing

¹⁾ Arch. f. exp. Path. u. Pharm., 51, 1904,

²⁾ Idem 71, 1913.

³⁾ Contrib. to Biology from the Amsterdam University 1914—15.

poison-influence, proved by the final appearance of normal, single, rapid contractions, we see, before this stage is reached, the second shortening becoming lower, of a shorter duration and appearing after a longer latent period; conversely it follows that a strong poisoning will be expressed by a high, prolonged, second shortening, having a short latent period and that the "fusion type" indeed corresponds with a stronger rate of poisoning than one with two tops, for with the former the latent period has reached its minimum, i.e. has grown equal to that of the first shortening; moreover the height is greater than that of a non-fusion second top. These magnitudes therefore, which may be expressed in the corresponding magnitudes of the first contraction, give a relative standard, holding for each separate muscle during the course of an experiment, for the poisoning at the moment of contraction, enabling us to picture to ourselves the progress of the poisoning, without our being dependent on the direct result, viz. the shape of the curve.

On studying the poisoning-process in this way, we notice in the series of curves peculiar differences, dependent on the concentrations, in which the poison has been applied.

1. In concentrations of 1:1000 and higher the muscle contracts as soon as it is brought into touch with the solution and maintains that shortening. On being stimulated the muscle shows either a very

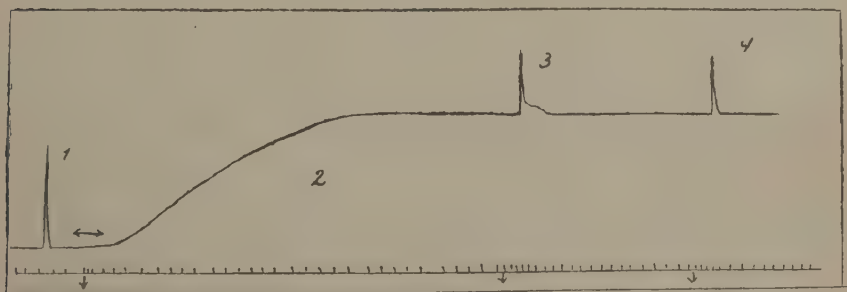


Fig. 1.

Experimental-process, when a veratrin-Ringer solution 1:1000 is poured on a muscle-nerve-preparation.

1: Contraction before poisoning: Af \longleftrightarrow : pouring on the solution. 2: subsequent contraction of the muscle; 3 and 4: contraction after electric stimulation, three, resp. six minutes after application of the solution: at \downarrow the cylinder stopped. Time $\frac{1}{6}$ sec.

slight veratrin-effect, or there is no result at all of the veratrin-poisoning, and the concentration is undistinguishable from the contraction yielded by an unpoisoned muscle on single stimulation.

(Fig. 1). This reaction is soon succeeded by complete insensibility for stimulation.

2. If the muscle has been put into a veratrin-solution weaker than 1:1000, but stronger than 1:100000 a series of curves is obtained, of which either the first or a following gives the strongest picture of the typical veratrin-poisoning, after which this effect diminishes till it finally disappears, so that the muscle, just as before the poisoning, responds to the stimulation with a single, rapid contraction, if at least it has not become insensitive, before this stage has been reached.

3. If solutions of 1:100000 and weaker are employed, a definite effect of the veratrin-action is obtained, which can maintain itself for hours together when the preparation is regularly stimulated.

There are three hypotheses which might explain the process described sub 1 and 2.

A. When the muscle has absorbed a certain quantity of poison and gradually diminishes the effect of this by its contractions — no matter how this happens — it is no more able to stand the influence of veratrin again.

B. The quantity of poison in the solution is not sufficient to supply the quantity abolished by the muscle.

C. In the period between two contractions the muscle modifies its character in such a way, that it grows less sensitive to veratrin-influence.

Hypothesis *A* may be omitted: a muscle once poisoned by veratrin can very well be influenced by veratrin-action again, after the veratrin-effect has been abolished by repeated contracting (e.g. by frequent stimulation), as the experiment teaches.

Hypothesis *B* may also be omitted, because VON FREY's¹⁾ experiments show, that minimum quantities are already sufficient to poison a muscle. Therefore the hypothesis remains, that the muscle alters its character in the period of time between two stimulations, a modification which can only be attributed to the action of veratrin, for if all circumstances are left unchanged and only the veratrin-concentration is altered, a definite rate of poisoning occurs, which appears to be constant (third process).

Evidently there exists, besides the veratrin-effect on the striated muscle, causing the well-known second shortening, another action, having an unfavourable influence on the effect first-mentioned, and causing a rapid and exhaustive effect in strong concentrations, in

¹⁾ Sitzungsber. der Physik.-Med. Gesellsch., Würzburg, 1912.

less strong ones a slow and gradual effect; while below a certain concentration it can no more occur.

If the poisoning-process in a calf-muscle, which is left in situ is studied here — again with a stimulation-interval of three minutes — the process mentioned sub 1 is never observed, because the veratrin-concentration in the blood never reaches a sufficient height. On employing large doses (e.g. 15 mgr. per 50 Gr. frog) the heart is arrested after a short time as BOEHM ¹⁾ describes it and the muscle is in no other relation — not considering a more intensive contact with the veratrin-solution — than in a muscle-trough of KEITH LUCAS, filled with a solution of the concentration at which the process mentioned sub 2 occurs; the conduct of the muscle is indeed in absolute accordance with this. On using smaller doses (1—2 mgr. per 50 Gr. frog), the heart, at least during the first hours after poisoning, keeps beating, only gradually diminishing its frequency; consequently the quantity of veratrin carried to the muscle is steadily increased and it should be borne in mind, that when the veratrin-concentration exceeds a definite threshold, the second effect of veratrin mentioned above will make its influence felt, i.e. the poisoning will seem less intensive: conversely every contraction will abolish part of the veratrin-effect and it may be supposed that in this way interference takes place between the influence of the two factors, determining the effect of the rate of poisoning, viz. the application and the rendering inactive of veratrin, when their two causes, i.e. the heart-action and the lapse of time between two contractions, occur in a definite proportion. As a result of this interference a periodicity occurs in the poisoning-process, i.e. the effects of stronger poisoning (higher, more prolonged second top) vary with those of less strong poisoning. At length the regularity of these oscillations is interrupted, because the heart-action diminishes under influence of the effect of the poison and the relation above-mentioned exists no more.

A constant poisoning in a muscle in situ can only then be obtained when the poison is applied without interference of the heart, e.g. by subcutaneous muscular injection (BUCHANAN ²⁾).

2. *Combination of veratrin and curare.*

DE BOER ³⁾ communicates the possibility of leaving only the second shortening by simultaneous application of veratrin and curare. He

¹⁾ Arch. f. exp. Path. u. Pharm., 71, 1913.

²⁾ Journ. of Physiol. 1899.

³⁾ Contributions Amsterdam 1914—15 and Zeitschr. f. Biol. 65.

gives few particulars however, so that I did not think it superfluous to repeat this experiment. It appears that quite different processes may arise, dependent on the lapse of time between the application of the two drugs.

A. If veratrin is first injected and the application of curare is put off till a distinct veratrinogram appears, the curare-injection remains without perceptible effect, the veratrin-poisoning proceeds as usual.

B. If curare is injected either simultaneously with veratrin-or so short a time after, that the veratrin-effect has not yet become manifest in the shape of a curve, in the further course of the experiment a typical veratrinogram appears, which shows that the two parts are equally effected by curare, so that both of them diminish till complete indirect insensibility; on direct stimulation the muscle even then gives a typical veratrinogram.

C. If veratrin is applied, if there is already an outspoken curare-poisoning, no veratrin-effect is shown, the poisoning behaves as a common curare-action till complete indirect insensibility.

D. If veratrin is injected while there are slight effects of the curare-action — it is of course impossible to mention objective data on this subject — in the further progress a veratrinogram appears with a usually very striking second top, which is afterwards modified into a normal-looking veratrinogram, which further behaves as such.

E. Finally veratrin may be injected between the stages C and D; then there arises neither a rapid contraction nor a veratrinogram, but a muscle-contraction, which should be identified the second shortening of the veratrin-curve. On direct stimulation there is also formed a typical veratrinogram in that case. (Fig. 2). The further process may lead to complete indirect insensibility, or to the fact that before this slow contraction there occurs a rapid one, causing another typical veratrinogram. In shape the shortening thus obtained is identical to the second contraction of a veratrinogram, when this succeeds the first in isolated condition, as it is sometimes seen during a poisoning-process.

Examined on a quick-turning cylinder its latent period appears to be twice or four times as long again as that of a normal single contraction; no top is formed, the highest part of the contraction is a horizontal line; the crescent is much less steep than the decrescent; the duration amounts to one to four seconds.

3. *Temperature.*

As to the influence of temperature, I agree in general with BRUNTON

and CASH¹⁾, according to whom both high and low temperatures have an unfavourable influence on the veratrin-phenomenon.

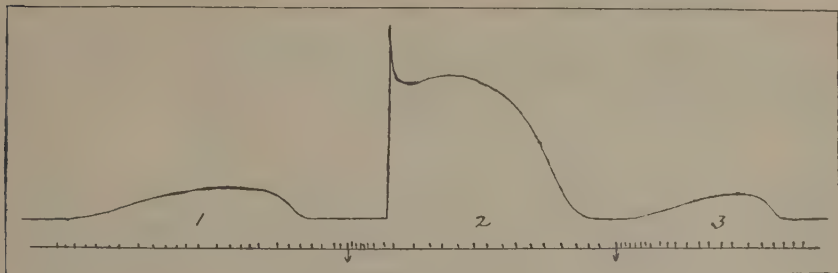


Fig. 2.

Combined action of veratrin and curare; 1 and 3: contraction on indirect stimulation; 2: contraction on direct stimulation; period between contractions: three minutes; at ↓ the cylinder stopped. Time $\frac{1}{5}$ sec.

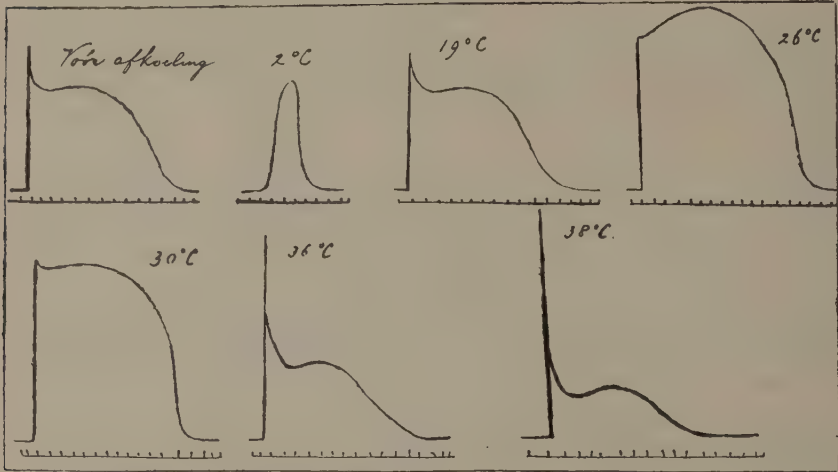
Here too a number of details are to be observed with respect to the modifications, the veratrinogram undergoes at various temperatures.

If a frog is cooled to 4° C. or lower and a veratrin-injection is given after that, no poisoning-effect is observed; the muscle behaves as an unpoisoned, cooled muscle, giving a relatively long and low contraction on induction-irritation. If the frog is subsequently heated, the second shortening gradually appears, first rapidly and of a short duration; above 14° C. the normal veratrinogram appears; conversely if a frog already poisoned is cooled, the second shortening disappears in quite the same way as it appears in the reverse experiment. Here too the cooled muscle behaves like an unpoisoned one. On heating above room-temperature the second shortening is seen to increase (in height as well as in duration). The first also increases its height as the contraction of an unpoisoned muscle would do, the second however increases more rapidly and consequently soon exceeds the first in size, so that a "fusion" type of curve arises.

At about 30° degrees the second shortening still increases in size, now however the first grows more rapidly and at $\pm 36^{\circ}$ the second shortening begins to decrease also absolutely, the first behaves exactly as the contraction of an unpoisoned muscle would do; till the muscle has become insensitive in consequence of heat-stiffness, there is still some veratrin-effect left. (Fig. 3). All this occurs quite independently of the poisoning-process; from every temperature with its corresponding

¹⁾ Journ. of Physiol. 1883.

curve-shape, we can return to room-temperature and see a typical veratrinogram arise.



Voor afkoeling = Before cooling.

Shapes of veratrinogram, yielded by one muscle at various temperatures. Time $\frac{1}{6}$ sec.

4. *Strength of stimulus.*

I have not succeeded in exercising an influence on one of the two parts of the veratrinogram separately by means of the strength of the stimulus. If the strength of the stimulus is gradually diminished, we may observe as MOSTINSKY¹⁾ describes, the critical progress of the excitability of the veratrin-muscle, i.e. below a definite limit, which is very exact, no reaction occurs on irritation, above this limit a reaction, differing but little from the maximal; moreover this always is a complete veratrinogram.

„A more detailed research concerning the problem of veratrin will appear in the „Archives de Physiologie Nêerl.””

¹⁾ loc. cit.

Anatomy. — "*The Problem of Orthognathism*". By Prof. L. BOLK.

(Communicated at the meeting of October 28, 1922).

In the meeting of February 1921 I called attention to the fact that the typically somatic human features are of a special character, viz, they are persisting fetal properties and conditions. I referred this fact to the influence of the endocrin system, which, through its inhibitive action, fixes fetal morphogenetic relations. The character of the human body, therefore, is its fetality, and this character results from what I am inclined to term a process of fetalization.

When studying the structure of the human skull from this point of view, it is surprising to note how all at once the whole complex of the typically human features, — and there are many in the skull — becomes easy of comprehension. Of all parts of the human body the head is most indicative of its fetal character. Earlier researches made by me had already favoured this view with regard to several of these properties. Long before conception of the fetalization-principle as the leading factor in the genesis of the human body as a whole, I had already pointed out that many somatic property of man represents an early stage of ontogenetic development.

However, there was one property of the skull about which I had no fixed opinion, and it is just this property that determines so emphatically the human physiognomy viz. its orthognathism. The question urged itself upon me, whether also this feature should be a persisting fetal property? I felt some diffidence in putting the question, as the pronouncements laid down in the literature were not very encouraging, the general conception being that the orthognathous (i.e. the human) skull-type has originated from the prognathous (i.e. the animal) type. The evolution is supposed to have consisted in a shortening of the jaws, in connection with the presumed reduction of the set of teeth. Now, to this conception objections might be raised also from other quarters, but I deemed it necessary, instead of opposing one speculation to another, to let the facts speak for themselves. This led me to an inquiry into the relation between prognathism and orthognathism. The results were indeed surprising, for not only was I in a position to establish this relation, but it also became evident that the whole complex of

human properties in the skull form one entity. However, in this paper I shall confine myself to my real subject.

My first attempt was to ascertain the essential morphological features of the prognathous and the orthognathous skull-type, for the criterion of short or long jaws is inadequate. With the aid of Figs 1 and 2 these features are easy to establish.

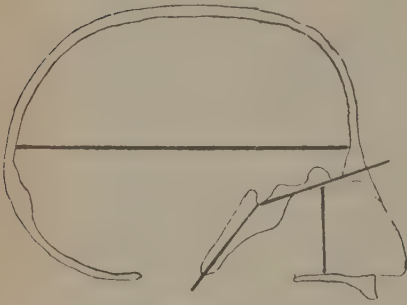


Fig. 1.

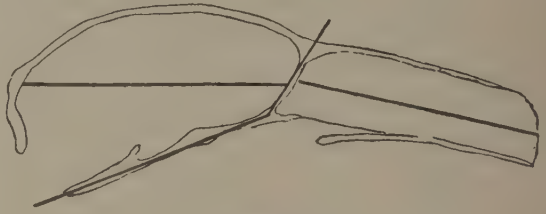


Fig. 2.

Fig. 1 shows a median section of a human skull. Fig 2 a similar section of the skull of Lemur, a Prosimia. Three lines have been drawn in both figures, viz the axis of the cranial cavity, the axis of the nasal cavity and the axis of the base of the skull. The three lines demonstrate in a simple way the essential features of the orthognathous and the prognathous skull-type. They are the following: In the orthognathous type the axis of the nasal cavity is approximately perpendicular to the axis of the cranial cavity, in other words the nasal cavity is situated beneath the cranial cavity; in the prognathous type, on the contrary, the axis extends more or less in the same direction as the axis of the cranial cavity. As to the axis of the base of the skull, it is flexed in either case, but in opposite direction. In the orthognathous type it is flexed between the basi- and the praesphenoid, an angle is formed with its open side turned anteriorly downwards. It is known in the literature as the sphenoidal angle. In the prognathous type the base is flexed between the praesphenoid and the ethmoid. An angle is formed with its open side turned posteriorly upwards. This angle I shall term the ethmoidal angle.

So it appears that the typical differences between the orthognathous and the prognathous skulls consist in the different situation of the nasal-cavity, either subcerebral or praecerebral, and in the different direction in which the base of the skull is flexed. The length of the jaws I do not consider as a fit criterion.

Now, when we test the skulls of the various classes of mammals by the criteria just mentioned, it appears that the whole class of the Primates, so not only man, is characterized by an orthognathous skull, in contradistinction to all the other mammalian classes. Applying the degree of prominence of the jaws as a criterion for prognathism is an erroneous method, which e.g. has led to the classification of apes among the prognathous forms. Though their jaws may be ever so much developed, the base of the skull never presents an ethmoidal angle, while the nasal cavity is never situated before the cranial cavity and in younger individuals there is even a sphenoidal angle. The strongly developed facial part of the skull in several apes, however, reminds us forcibly of a prognathous skull. These forms I will, therefore, distinguish as pseudopognathous.

In the foregoing the principle has been established for an inquiry into the relation between prognathism and orthognathism. The object of such an inquiry must be the answer to the question: which skull-type is the primitive one and which is the specialized type. First of all I will report the result of my examination of embryos of a number of mammals. It is the following: the fetus of all mammals is initially orthognathous, i.e. has a sphenoidal angle lacks an ethmoidal angle and the nasal cavity is subcerebral. Now, whereas this condition persists in apes partly and in man completely, in the other mammals the fetal orthognathous skull passes gradually into the prognathous type; first the sphenoidal angle disappears, then the ethmoidal angle is developed and coincidentally the nasal cavity rotates; its subcerebral position passes into a precerebral position. So it becomes evident that the orthognathous condition in man, which is the special feature of the human physiognomy, reveals itself again as a persisting fetal property.

Before demonstrating this in a series of embryos, I will briefly dwell on the fact that this transformation of the orthognathous skull into the prognathous type is a process with which we are confronted already in Reptiles, so that it has evidently been inherited by the Mammals from their reptilian ancestors.

Fig. 3 represents a median section through the head of an embryo of *Lacerta*, length of the head 4 mm. The chorda is still present, the vertebrae are not differentiated, likewise, the cranio-vertebral joint is still incomplete. Of the chondrocranium the basicranial plate enclosing the Foramen can be recognized. This plate extends frontad as far as the Hypophysis cerebri, which is still attached to the epithelium of the roof of the mouth. In front of the Hypophysis lies the prechordal plate. The latter presents two enlargements the one

turned upwards: the septum orbitale, and the other turned down: the septum nasale.

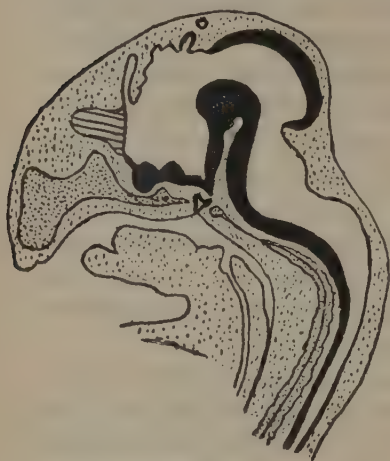


Fig. 3.

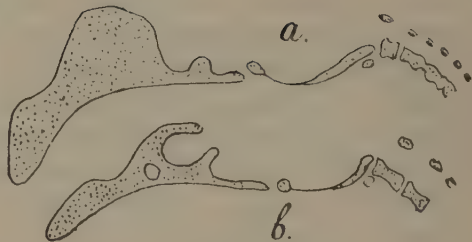


Fig. 4.

Now, two things should be observed: First that the prechordal plate extending in front of the Hypophysis, forms an angle with the basicranial plate behind it. This angle which is still more distinct in younger embryos, is identical with the sphenoida angle, the typical feature of the orthognathous human skull. The second thing to be observed is the direction of the septum nasale. In this young *Lacerta* embryo the axis of this septum is perpendicular to the base of the skull, which also is a typical feature of the orthognathous human skull. In passing, I wish to point out that in this phase of development the entrance to the mouth is, in *Lacerta*, not apical, but points downward. This reminds us incontinently of the permanent condition in *Plagiostomes*.

So the verticality of the septum nasale is a characteristic which, in this phase of development, the head of the *Lacerta*-embryo has in common with the orthognathous type. Fig. 4 shows how this type passes into the prognathous. In fig. 4^a the median section through a primordial cranium is given, head length 4.5 mm. In fig. 4^b the same with a length of 5 mm.; the enlargement in the two figures differs. Relative to the younger stage, the septum orbitale in the embryo with a head length of 4.5 mm. is considerably enlarged. It is clear that the axis of the nasal septum is no longer perpendicular to the base of the skull, but has rotated anteriorly. In the 5 mm. embryo this rotation is so considerable that the axis of the septum nasale is nearly on a level with the base of the skull. In this older embryo the septum orbitale exhibits marked signs of

resorption. So the figures 3 and 4 illustrate a rotation of the septum nasale, and consequently of the facial skull. From its original sub-cerebral position (orthognathism) it shifts into a precerebral position (prognathism). That in connection with this rotation plagiostomy changes into teleostomy we will pass over in silence, although this phenomenon would give ample scope for interesting observations.

It has thus been shown that the chondrocranium of Reptiles, in its early phase of development, resembles the orthognathous type. Now we are going to demonstrate that the process of development in Mammals bears a great resemblance to that of Reptiles. I have studied the ontogenesis of the skulls of a number of Mammals, and in all of them I met with the phenomena that I am going to describe for the skull of *Mus decumanus*.

Fig. 5 represents the median section of an embryo of *Mus decumanus* of 11.5 mm. In this stage the primordial cranium is



Fig. 5.

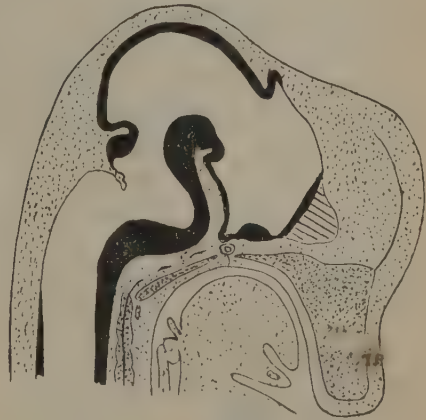


Fig. 6.

sufficiently differentiated. We will confine ourselves to the skeleton, omitting all further remarks that the following series of figures might suggest. In this stage the Hypophysis has become a closed vesicle, which, however, still adheres to the epithelium of the mouth. Behind the Hypophysis lies the basiscranial plate, which in *Mus* is subchordal over its whole length. Frontal to the Hypophysis lie the prechordal plate presenting a slight broadening dorsad, which is homologous with the strongly developed Septum orbitale in Reptiles. At its lower surface the Septum nasale is fastened. There is no denying that the basiscranial plate and the prechordal plate form an angle. This

angle, which we also found in *Lacerta*, is the sphenoidal angle that we know to be the typical feature of the orthognathous skull. Whereas the base of the skull is directed almost quite horizontally, the axis of the septum nasale is directed perpendicularly. Therefore in this stage of development the nasal cavity of *Mus* is subjacent to the cranial cavity. The skull of this young embryo of *Mus* possesses, therefore, two features, which are characteristic of the orthognathous skull, viz. a sphenoidal angle and a subbasal situation of the nasal cavity. That the latter condition is not the consequence of the intense development of the cerebral hemispheres, is borne out by the fact that in an early stage of development of Reptiles we find the same direction of the septum nasale. The condition in *Mus*, just described, is inherited from the reptilian ancestors of Mammals, which in their turn have inherited it from more primitive vertebrates. Plagiostomy, to which we referred heretofore, and which, to some extent, is encountered in the represented embryo of *Mus*, indicates in what direction we have to look for an explanation of this condition.

Accordingly we conclude that orthognathism is the characteristic of the young fetal mammalian skull. Now let us see how the prognathous type is developed from the primitive type.

Fig. 6 illustrates the median section through the head of an embryo of 13.5 mm. in length. The chorda begins to disappear, the Hypophysis lies within the cranial cavity, but is still attached to the mouth-epithelium. The base of the chondrocranium begins to stretch, but the sphenoidal angle is still recognizable. The axis of the septum nasale is still perpendicular to the prechordal plate.

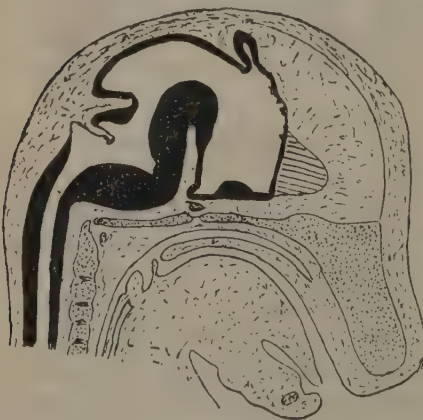


Fig. 7.

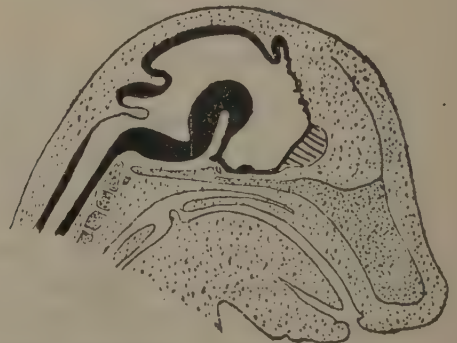


Fig. 8.

Fig. 7. Embryo of 20 mm. The basis cranii is stretched, the

sphenoidal angle has disappeared. The axis of the nasal septum is no longer vertical to the base of the skull, it has rotated, so that it forms an angle of 115° with the axis of the base of the skull.

Fig. 8. Embryo of 25 mm. The canalis Hypophyseos is closed, basal plate and prechordal plate have coalesced completely. The septum nasale has rotated further, and is inclined to the base of the skull at an angle of 130° , the part of this base to which the septum nasale is attached is bent slightly upwards, which is the first indication of the developing ethmoidal angle.

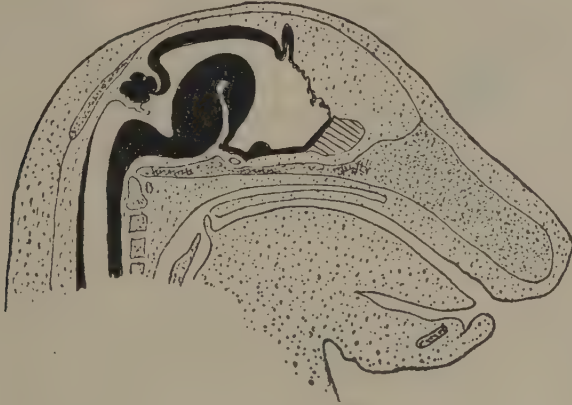


Fig. 9.



Fig. 10.

Fig. 9. Embryo of 35 mm. Three centra of ossification have appeared in the basis cranii for the Basisoccipitale, the Basisphenoid

and the Alisphenoid. The rotation of the septum nasale has continued; the nasal cavity now lies obliquely under and anteriorly to the cavum cranii. This rotatory movement apparently results from the further upward flexing of the frontal part of the basis cranii. The ethmoidal angle now becomes distinctly visible, right in front of the centrum of ossification of the Alisphenoid.

Fig. 10. Embryo of 43 mm. The ethmoidal angle has reached its definite value for the skull of the adult rat, the frontal part of the basis cranii has now become the anterior wall of the cranial cavity, the nasal cavity is situated before the cranial cavity, the skull has become prognathous.

It is evident, then, that the transformation from the orthognathous into the prognathous skull-type in the mammalian embryos is a regular process in which two succeeding phases are recognizable. In the first phase a straightening of the basis cranii takes place; the sphenoidal angle disappears. Its disappearance it attended with a change in the direction of the septum nasale, which is now placed obliquely to the base of the skull. After this the second fundamental alteration in the basis cranii commences, viz. the formation of the ethmoidal angle, the anterior (ethmoidal) portion of the base being turned up together with the septum nasale, which is attached to it. Consequently a part of the base of the fetal skull becomes the front wall of the cranial cavity.

I shall not enter into details concerning the various mammalian embryos that I have examined but will only add a few general remarks.

From the foregoing it is sufficiently evident that the orthognathous skull of man is to be considered as a persisting early fetal form. In stating this fact we have at the same time disproved the current opinion, that the sphenoidal angle, which is so characteristic of the human skull, is due to the intense development of the human brain. This angle, indeed, is not only a feature of all fetal mammalian skulls, but it occurs even in the chondrocranium of Reptiles. It is an essential character of, let me say, the primordial cranium of vertebrates in general. I shall not discuss this point any further.

The question now arises whether the intense growth of the Hemispheres has had no influence whatever on the anatomical relations of the skull, apart from the necessarily considerable enlargement of the cerebral crane. Such an influence, and even a very remarkable one, can indeed be demonstrated, as may be seen in comparing Fig. 11 and 12.

Fig. 11 shows the median section through the head of a dog's

fetus; length 32 mm.; Fig. 12 that of a human fetus 40 mm. long. The peculiarity I wish to lay stress on, regards the insertion of the

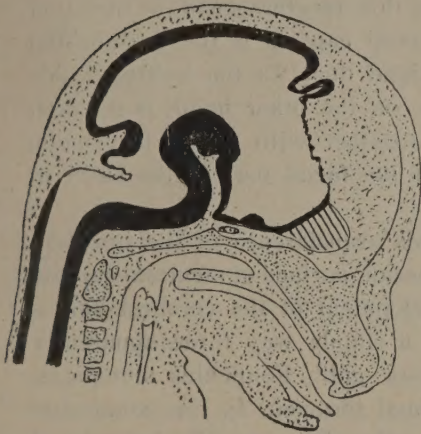


Fig. 11.

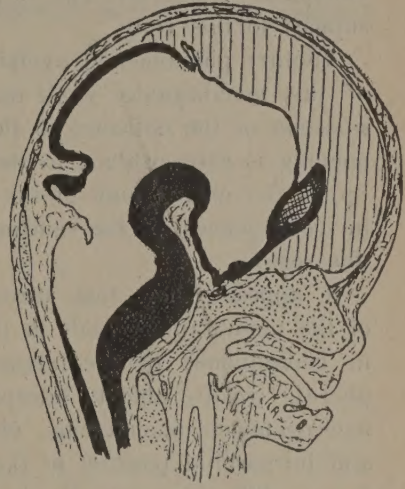


Fig. 12.

membranous vault of the crane on the cartilagenous nasal capsule. In the dog the former attaches itself to the acute border where the cranial base bends round in the nasal capsule, i.e. to the anterior margin of the cranial base. In man, on the other hand, it attaches itself in consequence of the intense development of the Hemispheres, to the anterior surface of the nasal capsule. It is obvious that a comparatively large portion of the nasal septum is hereby enclosed in the cranial cavity. This fact elucidates several phenomena observable at the human skull, I will only name them parenthetically. The shifting of the insertion of the membranous cranium to the anterior surface of the cartilagenous nasal capsule accounts for the occurrence of the *Crista galli*. This process, which is lacking in prognathous skulls is merely the top part of the nasal septum and the apex of the *Crista galli* indicates consequently the original frontal boundary of the base of the skull. This transference of the insertion of the membranous vault causes a shortening of the frontal part of the nasal region in man and it is quite obvious that the human physiognomy has been largely influenced by it. Earlier comparative anatomical inquiries already led me to conclude that the top part of the nose in Primates was reduced, and that the present boundary between nose and vault of the skull is of a secondary nature¹). The

¹) Die Herkunft der Fontanella metopica beim Menschen. Anat. Anz. Ergänzungsheft. Bnd 38. Jena 1911.

suture between nasal and frontal bones was lying on the forehead at the spot where in man not seldom the so-called Fonticulus metopicus is situated. The results of the embryological research lend support to this view.

Another phenomenon explained by this transference of the insertion of the membranous vault on the nasal capsule is the intra-orbital situation of the entrance to the lacrimal duct. In the half-apes this opening is extra-orbital; in the apes, on the other hand, it is taken up in the medial wall of the orbit together with the os lacrymale, in consequence of the shortening of the facial part of the skull in this region.

It appears then that through this transference of the insertion of the membranous vault to the anterior surface of the nasal capsule in consequence of the intense development of the cerebral hemispheres, we are able to interpret in a simple way three apparently heterogeneous phenomena, viz. Crista galli, Fonticulus metopicus, and intraorbital position of the lacrimal foramen. In this connection I may still add a remark about the other Primates. We have stated that apes, however much their jaws may project, possess in reality an orthognathous skull like that of man; they are to be classed as pseudopognathous. The persistence of the subcerebral position of the nasal cavity, also in apes, is the reason why the human physiognomy is ever more or less discernible in apes, which is to be ascribed chiefly to the position of the eyes. Originally the eyes of all mammalian embryos are disposed on the lateral surface of the head. In the prognathous type, in which the nasal cavity rotates before the cranial cavity the eyes retain their lateral position. In the orthognathous type, on the contrary, in which the nasal cavity persists under the cranial cavity the eyes can draw nearer to each other, and instead of the nasal cavity the orbitae occupy a precerebral position. Now this rotation obtains with all Primates, and this is why, physiognomically, apes resemble man.

In conclusion another point of similarity is the fact that all Primates possess a Crista galli, so in all of them the insertion of the membranous vault of the crane is transferred to the nasal capsule under the influence of the intense growth of the cerebral hemispheres, which is proved also by the intraorbital position of the foramen lacrymale in this class of mammals.

ERRATUM.

In these Proceedings Vol. XXV nos. 5 and 6, p. 202, line 15 from the bottom, to replace "*with respect to time*" by "*with respect to TEMPERATURE*".
